

THE SEPARATION OF CADMIUM AND COPPER SALTS
BY LIQUID-LIQUID EXTRACTION

by

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INTRODUCTION

The process of simple liquid extraction is a means of separation involving the relative solubilities or the distributional properties of a material between two immiscible liquids. If a solution of the material to be extracted is brought in contact with a second immiscible liquid, and the material has a preferential solubility in the second, an extractive transfer occurs between the liquids. After equilibrium is attained the two liquid phases are separated and the solvents recovered by distillation or another economical recovery system.

Instead of bringing the solution to be extracted and the extracting solvents together in single stage, it is also possible and sometimes advantageous to allow the contact to be of a multi-stage form with countercurrent flow of the solvents. A vertical tower is usually incorporated and the difference in specific gravities of the immiscible liquids passing through numerous mixing and calming sections allows both countercurrent flow and multi-stage contact. Thus, it can be seen that as the solvent flows up or down the tower, as the case may be, there is an enrichment or a stripping effect comparable to that of fractional distillation. Numerous designs and patented pilot-plant extractors have been created in recent years, but economically feasible industrial applications, the lack of ternary and polynary phase data, distribution coefficients for complex systems, and methods

of calculating equilibrium stage efficiencies have curtailed the advancement of the field.

Scheibel, designer of the apparatus used in this study, presented a method of stage calculation for a fractional extraction of isomers of chloronitrobenzene and several nonideal systems (18). Hixson and Smith (11) developed a method for predicting the quantitative performance of an agitator in liquid-liquid extraction systems. An equation was derived for weight of solute transferred from one phase to the other and verification was shown through a water-iodine-carbon tetrachloride system. Bartels and Kleiman (2) proposed a simplified mathematical approach for determining the effect of operating variables on liquid-liquid fractionation and presented equations and charts relating recovery and purification to the number of ideal stages and the feed point for fractional distribution coefficients between immiscible solvents. Methods of obtaining overall stage efficiencies, distribution coefficients, and overall performance data will be discussed more in detail in the section on Calculations.

The field of metallurgical extraction of inorganic salts from minor amounts of contaminating elements has been advanced by workers for the Atomic Energy Commission and others working on rare earth separations. Uranium metal, in an extremely pure form, has been obtained through an ethyl ether leaching-extraction of uranyl nitrate in water solution with concentrations of boron, cadmium, indium and salts of other elements. Both thorium nitrate and uranyl nitrate can be extracted and separated from

water solution by ether, owing to a difference in distribution coefficients (16, 19, 23).

Ferric chloride in aqueous solution has been extracted with isopropyl ether and studies for increasing the distribution coefficients with HCl in common ion effect have shown favorable results (10, 14, 15).

Garwin and Hixson (9) performed a separation of nickel and cobalt chlorides by extraction of the aqueous solution with capryl alcohol.

The liquid extraction method for separation of the rare earth metals has become a most important field, in recent years, since it eliminates the time consuming batch recrystallizations necessary under the older method. Through the work of Asselin and Comings (1), the separation of neodymium and thorium has been accomplished and separations of zirconium and hafnium, lanthanum, neodymium and neptunium from their impurities with ether (4, 6, 7, 21, 24), also have been performed by simple liquid extraction. There are potential possibilities in the pilot-plant extraction of other rare earth nitrates using water and hexanol (21) and various other organic solvents (3).

PURPOSE OF THE STUDY

The purpose of this research study was to obtain a high purity extraction process for the separation of cadmium salts from those of copper. With the increasing demand for purification

of certain metallic elements as set forth by the Atomic Energy Commission and interest extended by the paint pigment industries, this study was conducted to obtain a method of separation for high purification employing continuous flow equipment.

Most generally, cadmium salts are associated with the salts of zinc, lead, and copper, and metallic cadmium is recovered in an unpurified commercial form by the direct smelting of the sulfide ores. The sulfide mineralization of cadmium, called greenockite, occurs as a yellow strain or coating on lead and zinc ores of Joplin, Missouri, Southern California, and New Jersey. In the Kansas-Missouri district, zinc blend ores containing as high as 2.0% cadmium are associated with copper pyrites of concentrations of 0.1 - 3.0%. A 60 - 80% pure form of cadmium metal is obtained as a byproduct of the zinc distillation of these ores. Cadmium being more volatile, distills off in the first fraction and through a series of batch distillations-recrystallizations a 98% pure form may be obtained. In the case where there are contaminating elements in the zinc product, the ore is put into solution and the zinc is precipitated as the sulfide under controlled pH conditions. Cadmium is then precipitated from solution, but because of chemical similarity, copper contaminates the product. Introduction of an extraction step might prove economical in the zinc industry if employed between these two precipitation steps.

Another important resource for cadmium is the flue dust and waste products of the copper industry. Treatment of these ores

or the use of the flue dust material in acidic solution may prove feasible as a feed material in this extraction study.

It has been mentioned in the Introduction that several metallurgical systems have been tested in a liquid-liquid type of extractor. In some of these, separations of metal salts as high as 90 - 100% were obtained, giving a 99.9% pure metal after reduction. Knowledge obtained from these processes was applied to the system under study.

THE EXTRACTIVE-SEPARATION STUDY

An extraction process, regardless of the type method used or the equipment employed for study, can only perform extraction to the limit of the properties of the solvent or solvents used. Therefore, an extended study was performed to determine the solvents which would be most applicable to study for highest purification-separation of the copper-cadmium salts. Following the discussion on the Selection of the Solvents, a choice of equipment and method of analysis was outlined, in which purity and contamination were the major determining factors.

Selection of the Solvents

Since the salts of cadmium and copper were chosen as the materials to be extracted, and water was the most feasible heavy solvent, it became necessary to select an immiscible solvent

with a specific gravity of 0.8 or less which would exhibit preferential solubility for either the cadmium or copper salt. Solubility data for the nitrates, chlorides, sulfates, and acetates of cadmium and copper in organic solvents were obtained from Siedell's "Solubilities of Organic Compounds", Vol. 2, (19) and Perry's "Chemical Engineers' Handbook", 3rd ed. (17). These four anions were chosen because of their commercial importance and availability and the fact that one of the two metallic salts was noted to be quite soluble in a certain organic solvent. But a trial and error method would be required since the solubility of a selected salt could very well be affected both by the presence of water and the other metallic salt. A system for laboratory rough checks similar to that used by Garwin and Hixson (9) in the separation of nickel and cobalt, and by Weinhardt and Hixson (24) on the separation of vanadium and chromium, was employed.

Testing the cadmium and copper salts separately, it was found that both the aliphatic and the aromatic hydrocarbons (unsubstituted and substituted with nitro- and chloro- groups) were unsuitable as solvents and the solubility of the salts in the ethers was extremely low. A few of the aldehydes, esters and acids were tested but solubility was only moderate and the possibility of catalytic interaction during solvent recovery eliminated them from further exhaustive tests.

<u>Organic Solvent</u> <u>Name</u>	<u>Test Results</u> <u>Solubility</u>
Acetaldehyde	Negative
Benzaldehyde	Fair
Methyl Acetate	Negative
Ethyl Acetate	Negative
n-Butyl Acetate	Negative
n-Amyl Acetate	Poor
Acetic Acid	Negative
n-Butyric Acid	Poor
Propionic Acid	Fair

The alcohols and the ketones gave the best results with the solubility of the salts decreasing with an increase in molecular weight. Of the ketones, methyl isobutyl ketone and methyl ethyl ketone proved to be the better solvents, MEK having a greater solubility ratio (ratio of gms of cadmium or copper salt in MEK/gms of salt in H₂O) for each of the salts and MBK having a lower solubility with water (0.02 ml MBK/ml H₂O). In using these two solvents the sulfates and the acetates had to be eliminated as anions because of their low solubility and a possibility of a slow transfer rate which would require an additional number of equilibrium stages. The chlorides of cadmium, in a mildly acidic solution, formed an interesting white precipitate of complex organic nature with MEK and possibilities in this extraction combination had to be abandoned. After several trial runs with the metal nitrates and MEK the presence of an organic complex was noticed, which, because of its olive green color was believed to be suboxidic cadmium in form. This caused the discontinuation of ketones as a solvent.

The alcohols were decidedly the best solvents and secondary-butyl alcohol was chosen from the standpoints of importance and its preferential solubility of cadmium over copper salts. It was found that the copper salts were insoluble in pure SBA. Through several tests on various salt concentrations, it was concluded that in mixtures of water - SBA - copper nitrate (in equilibrium), the concentration of the copper nitrate in the upper layer (SBA) was directly proportional to that in the lower layer (H_2O) only to the extent of the amount of H_2O in the upper layer (the solubility of H_2O in SBA at $20^{\circ}C$ is 22.5 ml/100 ml). Therefore, it was believed that extraction might be possible if the concentrations of the nitrates (or the chlorides as later shown) were moderately dilute. But dilution created another problem. The cadmium salt, receiving little opposition from the dilute copper salt, lost its preferential solubility in the SBA and both salts remained in aqueous solution. A logical explanation for the cause of this problem was discussed at length by Garwin and Hixson (9) referring to cobalt chloride.

Preliminary qualitative experiments yielded the result that cobaltous chloride in dilute aqueous solution is not extracted at all by capryl alcohol; it is only as saturation is approached that the alcohol layer takes on light blue tint, indicating the presence of some cobaltous chloride. The cobalt was extracted best from dark blue aqueous solutions and not at all when the aqueous phase was red. In the former case the alcohol layer turned blue, in the latter it remained colorless. Of the hypothesis which explain these effects ... the facts tend to support the hydration hypothesis. (That the degree of hydration produces a color change of the ion.)

Therefore, in the extraction of a dilute solution of cobaltous

chloride it is essential that a blue aqueous solution be obtained through some manner for reducing the degree of hydration.

Studies were continued on the effect of the addition of various foreign electrolytes in the belief that the presence of these electrolytes in solution would render the cobalt salt less hydrated and hence make possible its extraction by the alcohol.

It was found that these electrolytic additions to the dilute cobaltous chloride solution classified themselves into three groups:

- (A) Those which produced a gradual color change from red through violet to dark blue.
- (B) Those which produced a red to darker red color change.
- (C) Those which produced a detrimental reverse color change from blue to red or from violet to dark red.

Hydrochloric acid and calcium chloride, being a type (A) electrolyte, were employed with favorable results in the Garwin-Hixson cobalt-nickel extraction.

From these studies and from other articles on electrolytic behavior it was believed that an electrolyte must be added if an extraction of dilute solutions of cadmium and copper salts was to be accomplished. A list of possible electrolytes for this dehydration was obtained from the literature (1, 13, 24) and through trial and error methods, noting the solubilities of the compounds, calcium carbonate was chosen. The carbonate was selected in view of its extremely low solubility (0.0012 gm/100 ml of H_2O) and its interference in the analysis of the products would prove negligible.

Equipment

The liquid extraction column used in this research study was a two-inch laboratory extractor designed by Scheibel of Hoffmann-La-Roche, Inc., and constructed by the Otto H. York Company of East Orange, New Jersey (Plate I). The column casement was two inch pyrex pipe with flanged caps of Teflon and stainless steel at the ends, and 3/8 inch pyrex tubing placed along the column for proper liquid introduction (Plate II). The internal structure, all of stainless steel, consisted of alternate calming and mixing sections with a centrally located shaft upon which were mounted vertical blade agitators. The calming section was a four inch cylinder of loosely woven stainless steel wire mesh which served as an entrainment separator for the immiscible liquids. The mixing section was a one inch open area with the agitator blade in the center. At the top of the column, coupled to the agitator shaft, was a one-twentieth horse-power air driven motor which maintained a constant rotary speed under a given air pressure and a somewhat constant load. A tachometer was attached to the upper end of the motor enabling a constant check of the rotor speed during the runs. Pressure on the air line was regulated by a diaphragm air control and a 3/8 inch needle valve.

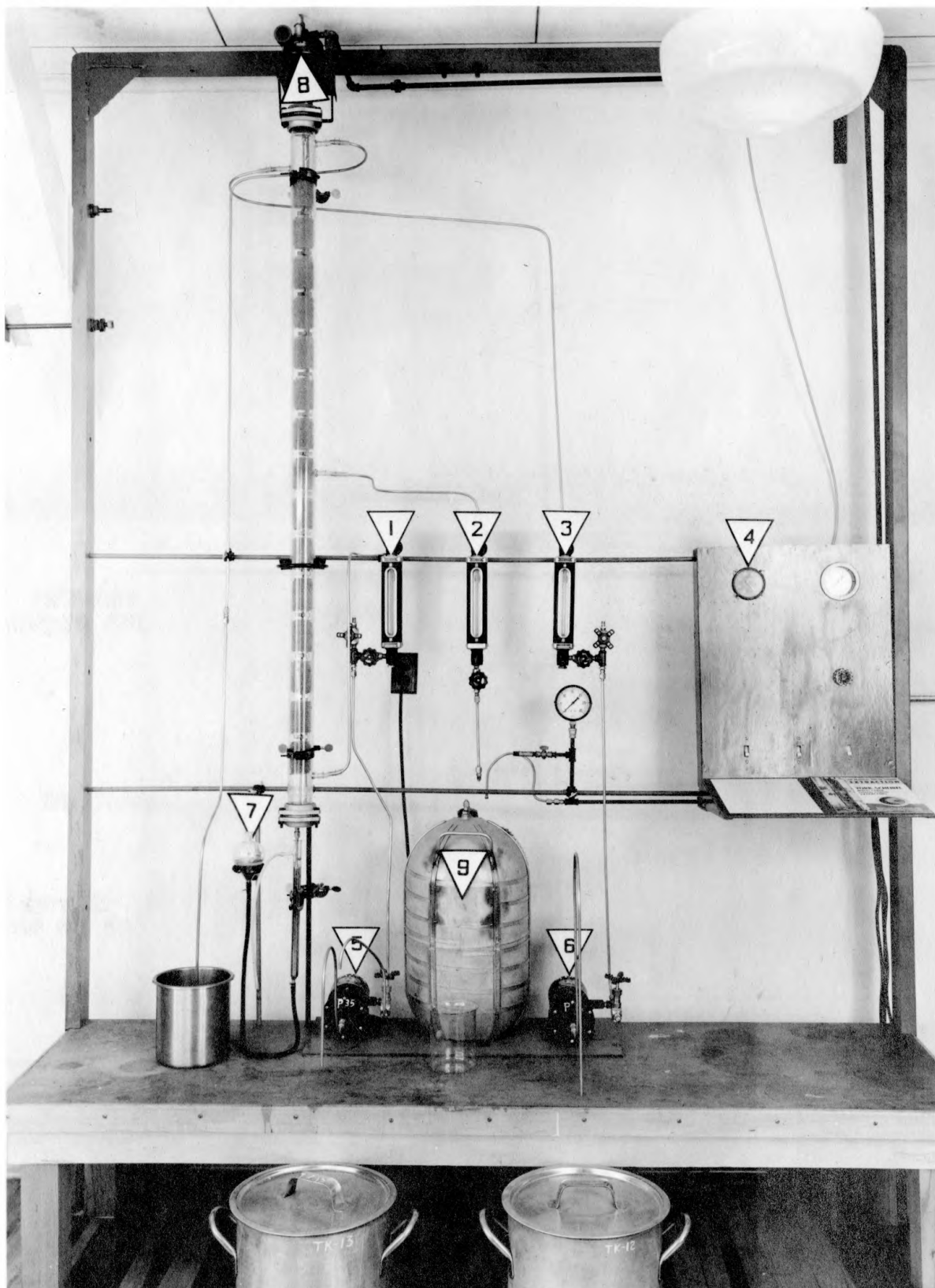
Three Fischer-Porter flowrators indicated the rate of the liquid feed and each of the two solvents flowing to the column at their proper introduction points. Mounted upstream from the flowrators of the two immiscible solvents were two one-half horse-power

EXPLANATION OF PLATE I

York-Scheibel Liquid Extractor

1. Flowrater for lighter solvent.
2. Flowrater for feed solution.
3. Flowrater for heavier solvent.
4. Tachometer.
5. Light solvent centrifugal pump.
By-pass valve to the right of the motor.
Control switches on the board at the right.
6. Heavier solvent centrifugal pump.
7. Mercury manostat.
8. Air motor connected to agitator shaft.
Air line pressure indicator and valve on
the board at the right.
9. Feed tank.
Feed line to the flowrater and air pressure
line for maintaining a constant head in the
tank are above the tank.

PLATE I

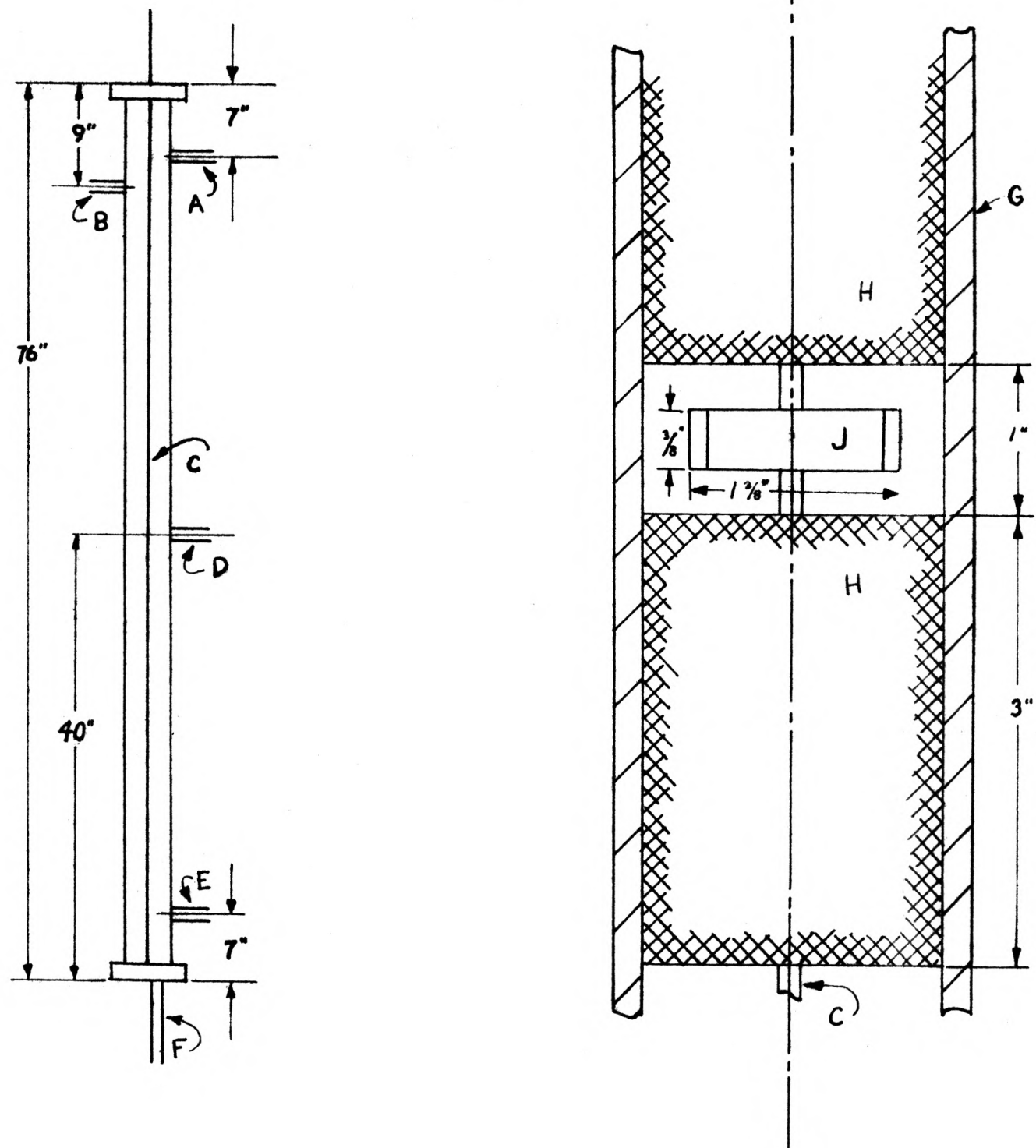


EXPLANATION OF PLATE II

Liquid-liquid Extractor Dimension Diagram and Detail of One Complete Stage

- A. Outlet for the Lighter Liquid (SBA).
- B. Inlet for the Heavier Liquid (H_2O).
- C. Agitator Center Rod ($1/4$ inch) Stainless Steel Rod.
- D. Feed Inlet.
- E. Inlet for the Lighter Liquid.
- F. Outlet for the Heavier Liquid.
- G. Glass Pipe (2 inch Pyrex).
- H. Stainless Steel Wire Mesh Entrainment Separator.
- J. Stainless Steel Agitator Blade.

PLATE II



Dimension Diagram of the Column

centrifugal pumps for maintaining a continuous flow and a constant head. A stainless steel pressure feed tank was upstream to the feed flowrator and flow was accomplished by maintaining a five pound per square inch air head in the tank. All of the connection lines were 1/4 inch stainless steel tubing. The 1/4 inch control needle valves and their threaded tube adaptor fittings were of 316 stainless steel. The connections between the glass inlets of the column and stainless steel tubing were 1/4 inch Tygon tubing. A mercury manostat at the bottom outlet of the column offered a finger-tip control of the height of the interface. Four five-gallon 316 stainless steel kettles were employed as solvent reserviors and product collectors.

The greater part of the equipment which came in contact with the solvents or the metallic salts was either glass or stainless steel. These two materials were selected to eliminate the possibility of contamination of the solvents or corrosion of the equipment. A 316 stainless steel steam heated batch still with water cooled condenser was employed for solvent recovery.

Analysis of the Products

The analysis of the products, both in the upper (SBA) layer and the lower (H_2O) layer, was accomplished by the use of a Beckman pH meter, Model H-2 with glass electrode (Fig. 1).

This instrument gave an immediate pH reading (in a range from 0 to 14 pH) when the two electrodes were emerged in unknown sample



Fig. 1. Beckman pH Meter - Model H-2. The essential parts of the pH Meter are the calomel reference electrode (1), the glass electrode (2), the temperature correction control (3), range selector switch (4), the calibration control (5), and the indicator dial (6).

solution. A 7.00 ± 0.004 pH buffer solution was used to calibrate the meter.

The method of analysis is explained in full by Fales and Kenny (5) in a paragraph entitled "Potentiometric Titrations Involving Precipitation." The titrating solution was 0.10 N sodium hydroxide. The concentrations of the cadmium and the copper salts were obtained by plotting pH against the number of milliliters of 0.10 N NaOH added to the test sample (Plate III).

The number of milliliters necessary to precipitate the total amount of cadmium salt (precipitating in the 4.0 to 5.5 pH range) and the copper salt (precipitating between 4.0 and 8.0 pH) was found by estimation of the values between the extrapolated slope line intersections. From Plate III on a test sample of 10 ml, the amount of 0.10 N NaOH needed to precipitate the Cd salt was 2.55 ml, and for the Cu salt was 5.00 ml. In grams of salt present, this became:

$$\text{Cd (2.55) (0.0001) (1/2) (236.43) = 0.0314 gm}$$

$$\text{Cu (5.00) (0.0001) (1/2) (187.58) = 0.0469 gm}$$

For the study itself, the unit of gm/ml of solvent product was employed.

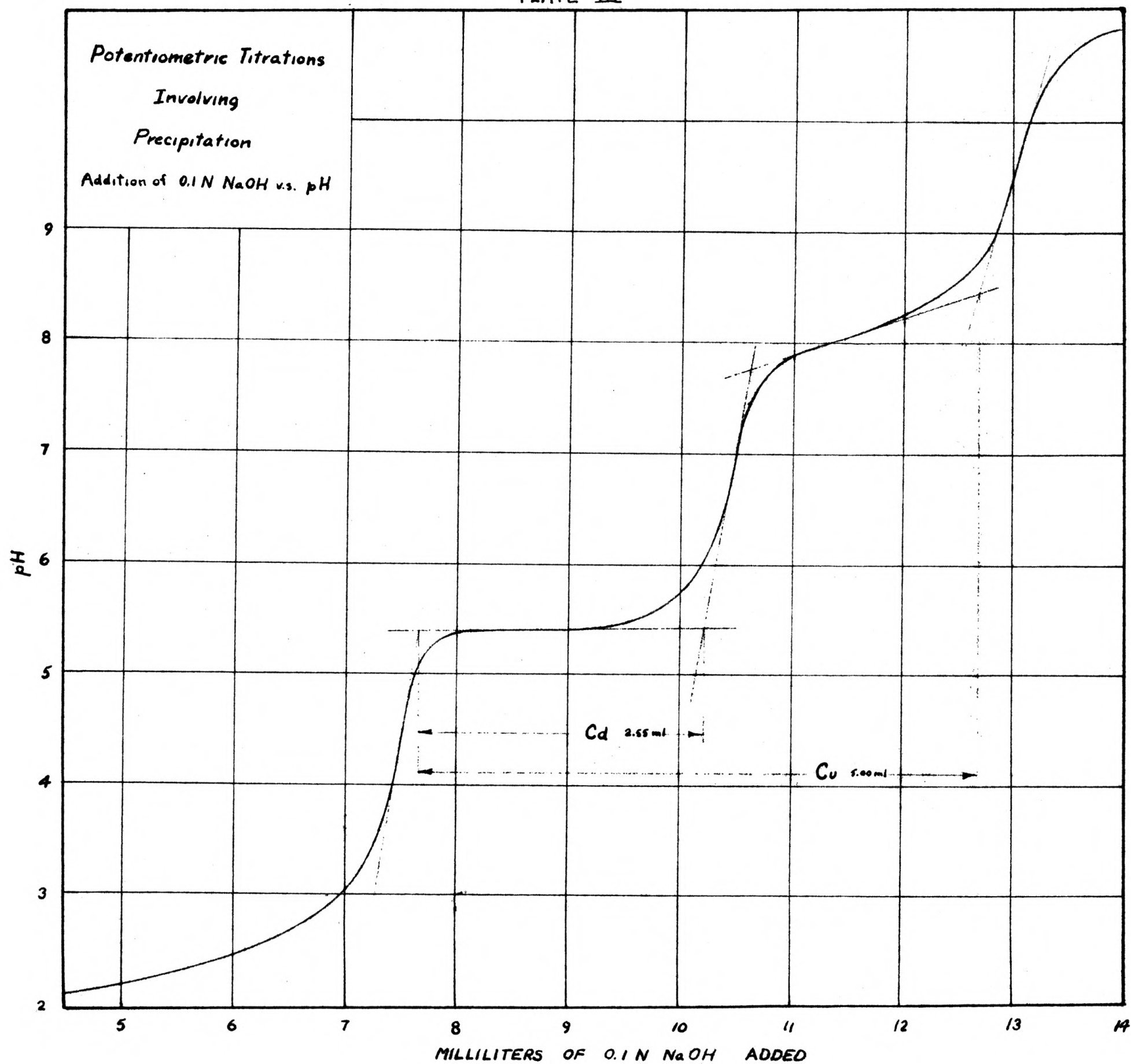
RUN PROCEDURE

Eight extraction runs were made in this study, and a uniform procedure was followed throughout. The volume of feed was determined by a calibrated flowrater and the composition predetermined in the make-up. The water phase, saturated with

EXPLANATION OF PLATE III

Potentiometric Titrations
Involving
Precipitation

PLATE III



calcium carbonate, was introduced into the column (H_2O saturated with CaCO_3 at the top and SBA at the bottom, Plate II) through a calibrated flowrater as was the secondary butyl alcohol. Since the solvents used were the products obtained from distillation-solvent recovery, both the SBA and the H_2O were split equilibrium phases and of course were interchangeably saturated.

In starting-up, the column was filled with both solvents so that the interface of the liquids was at the mid-point with the solvent rates being constant. The agitator speed was set and recorded. Feed was then introduced and a minor adjustment of the manostat was made for a change in the height of the interface. Check was made from time to time to insure that the speed and rates were constant. At the end of one hour, samples of the top and bottom products were taken and the speed and rate constants were changed. Equilibrium was assumed to be established in a one hour period. This time assumption was well in excess of the required time to obtain equilibrium in single stage equilibrium tests. Another sample was taken at the end of a second hour and the apparatus was then emptied and cleaned. The products and the remaining solvents were distilled and prepared for the next run, after recording their total volume.

In this type of extraction column the height of the calming section was fixed in the design. Therefore, for a given calming section height there must exist an upper limit for the agitator speed above which the separation will become incomplete. At this point the droplets in the coalescent phase fail to divide in

their transfer from stage to stage. In this work the upper limit of the agitator speed was found to be 300 R.P.M. The interface between the solvents was a coalescent - SBA interface at the top and a coalescent - H_2O interface at the bottom of the column. It was essential that none of the coalescent fraction be removed from the column as products.

The samples of the upper and lower products were evaporated to dryness, and then made acidic with HNO_3 . The total amount of Cu and Cd salts present in the products was determined by potentiometric titration with 0.10 N NaOH in the manner described in Analysis of the Products. Tabulation of the results for all eight runs may be found on Table 1. Potentiometric Titration Data for the lower and upper layer products may be found in the Appendix on data Tables 2 and 3, respectively.

An overall material balance was outlined for Run 16-1 on a weight percentage basis (Appendix), and since this method of calculation offers no indication as to the degree of extraction existing at each stage, Scheibel's method for individual stage calculation was employed.

Table 1. Run procedure data and the results of the potentiometric titrations.

Run	Trial	Feed Material	Agitator Speed (R.P.M.)	Rate H_2O ⁺ (H_n) ml/sec	Rate SBA (L_n) ml/sec	$\frac{H_n}{L_n}$	(H_m) ⁺⁺	$\frac{L_m}{H_m}$
13	1	Cu & Cd (Cl)	200	1.057	1.673	0.631	1.157	1.458
	2	Cu & Cd (Cl)	200	1.077	1.743	0.616	1.177	1.465
14	1	Cu, Cd (Cl) (HCl)	225	0.843	1.266	0.665	0.843	1.346
	2	Cu, Cd (Cl) (HCl)	250	0.900	1.464	0.615	1.000	1.464
15	1	Cu, Cd ($(NO_3)_2$)	220	0.775	1.380	0.561	0.875	1.579
	2	Cu, Cd ($(NO_3)_2$)	230	0.775	1.380	0.561	0.875	1.579
16	1	Cu, Cd ($(NO_3)_2$)	150	1.775	2.29	0.775	1.875	1.222
	2	Cu, Cd ($(NO_3)_2$)	300	1.775	2.29	0.775	1.875	1.222

+ H_2O phase was saturated with $CaCO_3$

++ $H_m = H_n + 0.10$

The flow rates for the H_2O and the SBA entering the column were obtained by direct calibration of the flowraters. The values H_n/L_n and L_m/H_m are units to be used in Scheibel's Equations. The Upper layer refers to the SBA products layer and the Lower layer refers to the H_2O products layer.

Potentiometric Titration Results

Lower Layer Cd Salt		Upper Layer Cd Salt		Lower Layer Cu Salt	
Run	gm Cd Salt ml of H_2O	Run	gm Cd Salt ml of SBA	Run	gm Cu Salt ml of H_2O
13-1	0.000532	13-1	0.005125	13-1	0.006820
13-2	0.002979	13-2	0.009014	13-2	0.011372
14-1	0.004220	14-1	0.014532	14-1	0.009295
14-2	0.002216	14-2	0.017228	14-2	0.018148
15-1	0.004327	15-1	0.006256	15-1	0.009375
15-2	0.006438	15-2	0.004847	15-2	0.012662
16-1	0.001960	16-1	0.002145	16-1	0.007050
16-2	0.003140	16-2	0.003200	16-2	0.009190

CALCULATIONS AND INTERPRETATION OF THE DATA

Calculations for the composition of the top and bottom products were accomplished by using the potentiometric titration method and converting milliliters of 0.10 NaOH to equivalent weight of salt and dividing through by the number of milliliters of sample taken.

Potentiometric Titration Calculations

Sample Calculation Run 13-1

From Tables 2 and 3 plots of pH versus the number of milliliters of 0.10 N NaOH were constructed (Plate IV) for both the upper and lower layers. Plate V is a plot for Run 13-2 and a similarity in the method of analysis may be noted. Interpolating in the manner described in the Analysis of the Products for Run 13-1 the points,

$$A = 1.61 \text{ ml}$$

$$B = 17.22 \text{ ml}$$

$$A' = 6.31 \text{ ml}$$

$$B' = 8.23 \text{ ml}$$

$$D' = 28.65 \text{ ml}$$

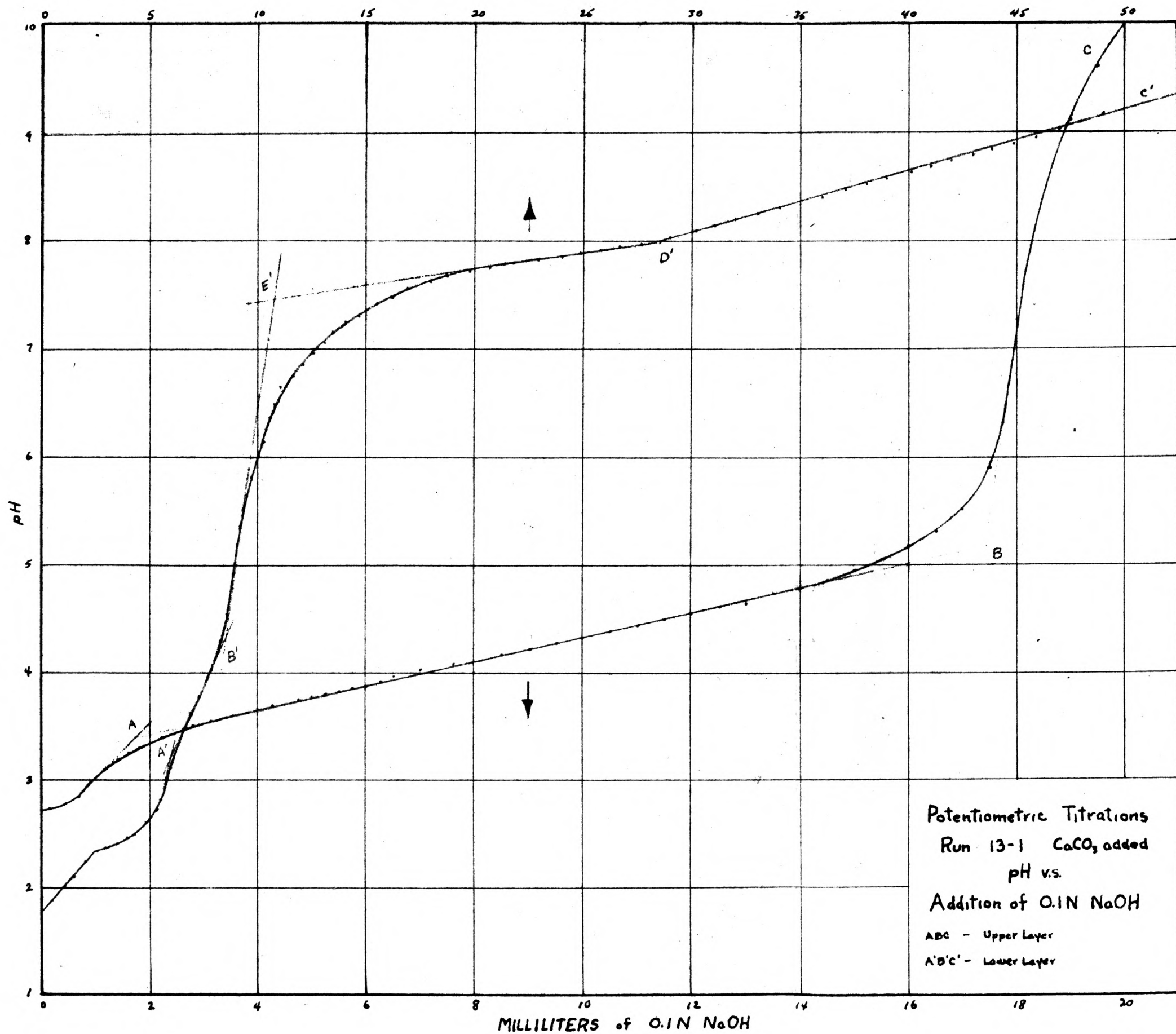
were determined. The amount of sample taken was tabulated at the top of the data column. This value was 36 ml for Run 13-1. Converting by equivalent weights,

$$\frac{(17.22 - 1.61) (0.0001) (1/2) (236.4)}{36} = 0.005125 \quad \begin{array}{l} \text{gm Cd salt} \\ \text{ml SBA} \end{array}$$

EXPLANATION OF PLATE IV

Plot of the Potentiometric Titration on Run 13-1
pH versus the number of ml of 0.1 N NaOH added.

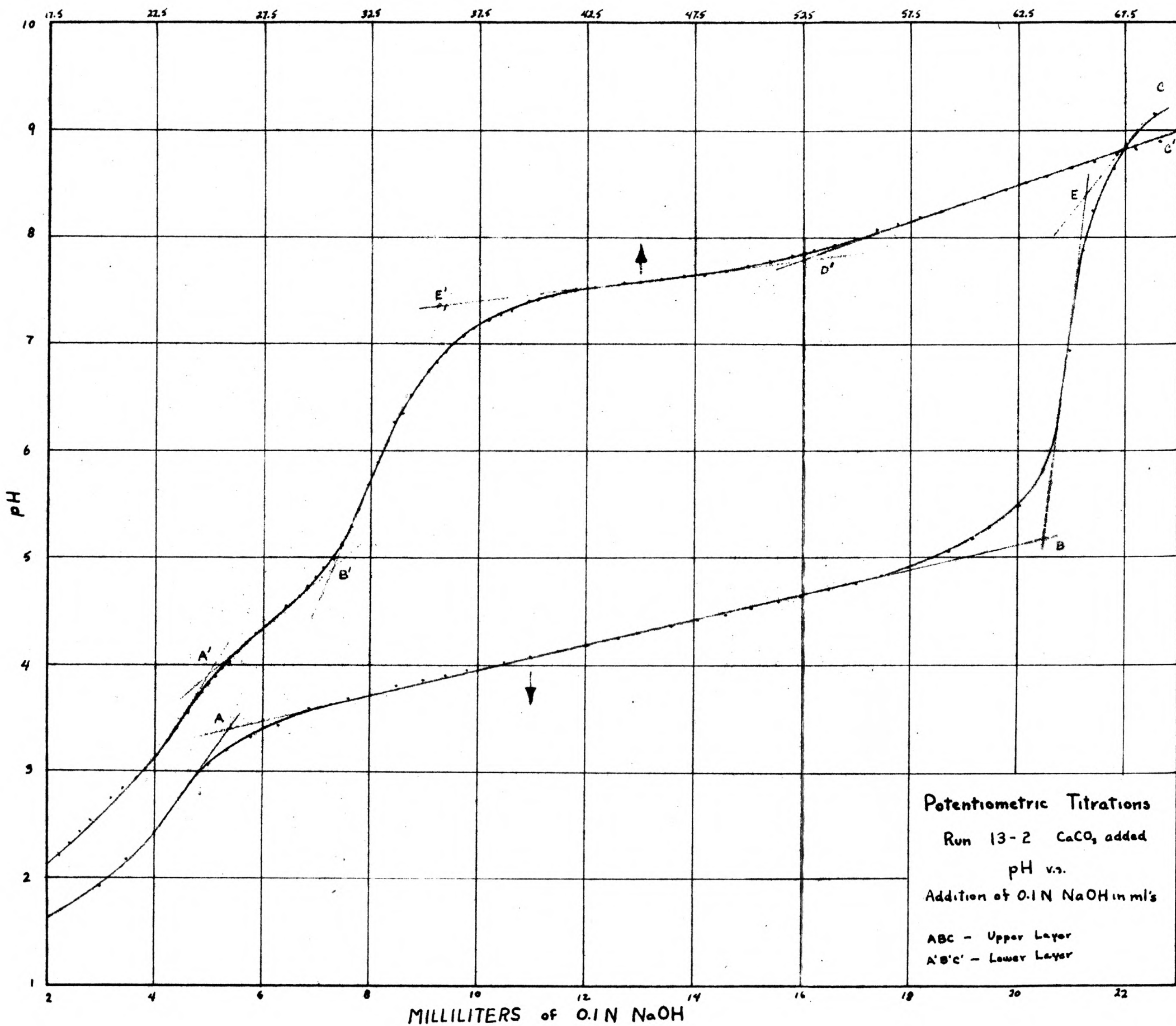
PLATE IV



EXPLANATION OF PLATE V

Plot of the Potentiometric Titration on Run 13-2
pH versus the number of ml of 0.1 N NaOH added.

PLATE V



$$\frac{(8.23 - 6.31) (0.0001) (1/2) (236.4)}{36} = 0.000532 \frac{\text{gm Cd salt}}{\text{ml H}_2\text{O}}$$

$$\frac{(28.65 - 6.31) (0.0001) (1/2) (187.58)}{36} = 0.005820 \frac{\text{gm Cu salt}}{\text{ml H}_2\text{O}}$$

The results of the calculations for this run, and the other seven, may be found on Table 1. It has been mentioned that the concentration of the copper salt in the upper layer would be in proportion to the amount in the H₂O layer on the top most stage, and present only to the extent of the solubility of H₂O in SBA. It was impossible to detect any copper in the upper layer samples by this method of analysis, so an average distribution coefficient of 0.45 was estimated from experimental equilibrium data, and a theoretical concentration was determined for the Stage Calculations.

Stage Calculations

In order to correlate the material so as to approximate the number of stages necessary for economical industrial application, and to obtain some indication of the performance of the column with fifteen actual stages in respect to fifteen theoretical equilibrium stages, the method suggested and outlined by Scheibel (18) was employed. A relationship for the equilibrium-stage calculations was derived in a manner parallel to that employed in distillation calculations.

Let,

L_n = flow rate of lighter liquid

H_n = flow rate of heavier liquid

Y = concentration of the salt in the lighter liquid

X = concentration of the salt in the heavier liquid

Above the feed,

$$\text{Input} = H_n X_t + L_n Y_{n+1}$$

$$\text{Output} = H_n X_n + L_n Y_t$$

Balance,

$$H_n X_t + L_n Y_{n+1} = H_n X_n + L_n Y_t$$

At a given concentration, based on the same liquid concentration as X and Y ,

$$Y_n = D_n X_n$$

And, for the $n+1$ stage (Plate VI),

$$\begin{aligned} Y_{n+1} &= \frac{1}{L_n} \left[\frac{H_n Y_n}{D_n} + L_n Y_t \right] \\ &= \left[\frac{H_n}{L_n D_n} \right] Y_n + Y_t \end{aligned}$$

And, for the stages below the feed,

$$X_{m+1} = \left[\frac{L_m D_m}{H_m} \right] X_m + X_B$$

When D_n and D_m are independent of concentration,

$$\begin{aligned} Y_2 &= \left[\frac{H_n}{L_n D} + 1 \right] Y_t \\ Y_3 &= \left[\frac{H_n}{L_n D} \right] \left[\frac{H_n}{L_n D} + 1 \right] Y_t + Y_t \\ &= \left[\left(\frac{H_n}{L_n D} \right)^2 + \frac{H_n}{L_n D} + 1 \right] Y_t \end{aligned}$$

EXPLANATION OF PLATE VI

Material Balance on the Column

Nomenclature for Data Calculations

- x = The stage number as a power of subscript.
- n = Top stage (The same as t in the material balance, and equal to x-1 when Y values are being calculated.)
- m = Bottom stage (The same as sub-B in the material balance, and equal to x-1 when X values are being calculated.)
- H_n = Flowrate (gm/ml) of the heavier liquid entering.
- L_n = Flowrate (gm/ml) of the lighter liquid leaving.
- H_m = Flowrate (gm/ml) of the heavier liquid leaving.
- L_m = Flowrate (gm/ml) of the lighter liquid entering.
- X = Grams of salt per milliliter of heavier solvent.
- Y = Grams of salt per milliliter of lighter solvent.
- D = Distribution coefficients equal to Y over X.
- D_e = Distribution coefficients for the cadmium concentration in the stages above the feed, determined from Plate VII.
- D_f = Distribution coefficients for the cadmium concentration in the stages below the feed, determined from Plate VII.
- A = The value $\frac{H_n}{L_n D}$ for Scheibel's equations.
- B = The value $\frac{L_m D}{H_m}$ for Scheibel's equations.

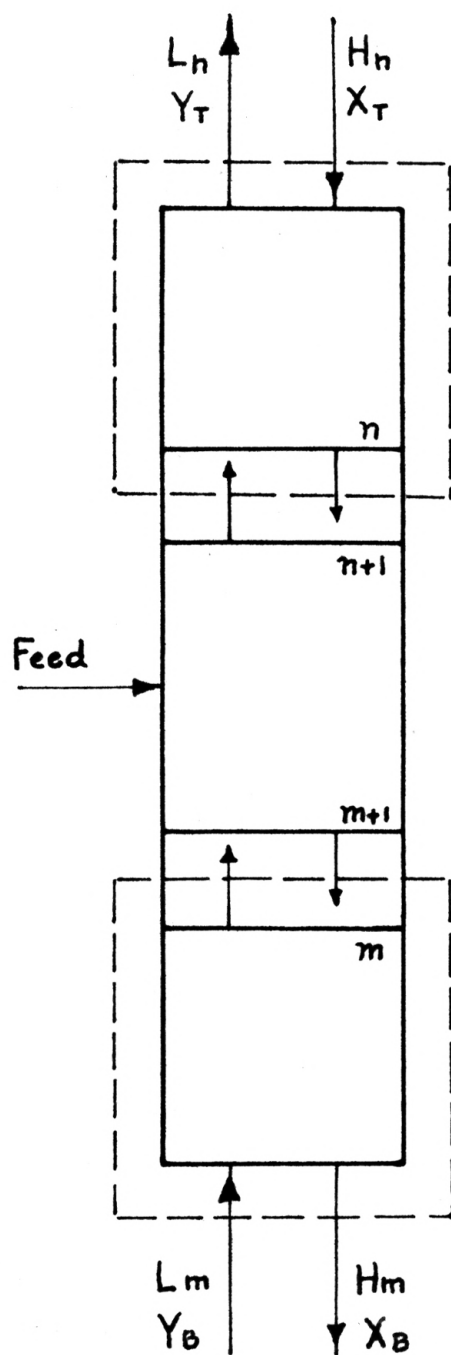


PLATE VI

This forms a simple geometric progression such that for any Y value,

$$Y_{n+1} = \frac{\left(\frac{H_n}{L_n D}\right)^{n+1} - 1}{\left(\frac{H_n}{L_n D}\right) - 1} Y_t \quad (1)$$

In a similar manner, it can be shown that,

$$X_{m+1} = \frac{\left(\frac{L_m D}{H_m}\right)^{m+1} - 1}{\left(\frac{L_m D}{H_m}\right) - 1} X_B \quad (2)$$

An additional notation in the nomenclature for the data includes,

$$A = \frac{H_n}{L_n D}, \text{ and } B = \frac{L_m D}{H_m}$$

In the solution for X and Y values, it should be noted that sub-x in the data designates the stage number (n+1) in the equation above, assigning values down from the top for Y and up from the bottom for X, in the case of (m+1).

Sample Calculations for Run 16-1, Cu and Cd calculations on stage 2, upper and lower layers.

Cu Calculation

From Table 1,

$$\frac{H_n}{L_n} = 0.775 \text{ and } \frac{L_m}{H_m} = 1.222$$

It might be noted that,

$$H_m = H_n + 0.10$$

for all runs, since the concentration and the flow rate of the feed was predetermined to simplify the calculations. Since the concentration of the copper nitrate in the lower layer was found to be proportional to the amount in the upper layer to the extent of the solubility of H_2O in SBA, an average distribution coefficient (D) was estimated for use in all Cu calculations.

$$D = 0.45 \quad x = 2$$

$$A = \frac{H_n}{L_n D} = \frac{0.775}{0.45} = 1.722$$

$$A^x = (1.722)^2 = 2.970$$

$$A^x - 1 = 1.970$$

$$A - 1 = 1.722 - 1.000 = 0.722$$

$$Y_t = 0.00705 (0.45) = 0.00317 \text{ gm/ml, using equation (1),}$$

$$Y_2 = \frac{A^x - 1}{A - 1} Y_t = \frac{1.970}{0.722} (0.00317) = 0.00865 \text{ gm Cd/ml SBA}$$

calculating for the lower stage 2 using equation (2),

$$D = 0.45 \quad x = 2$$

$$B = \frac{L_m D}{H_m} = 1.222 (0.45) = 0.546$$

$$B^x = (0.546)^2 = 0.298$$

$$B^x - 1 = -0.702$$

$$B - 1 = -0.454$$

$$X_B = 0.00705 \text{ gm/ml}$$

$$X_2 = \frac{B^x - 1}{B - 1} X_B = \frac{-0.702}{-0.454} (0.00705) = 0.01090 \text{ gm Cd/ml } H_2O$$

In a like manner the calculation of other X and Y values for the

different stages were computed (Tables 4 and 5 in Appendix).

Cd Calculation

The ideal situation involving a constant distribution coefficient, or the use of an average value of D could not be employed in the Cd salt calculations since the distribution coefficient varies with the total cadmium concentration and the amount of copper in solution. An equilibrium diagram (Plate VII) was constructed from experimental data, plotting the concentrations of $\text{Cd}(\text{NO}_3)_2$ between SBA and H_2O (saturated with CaCO_3) with constant concentrations of $\text{Cu}(\text{NO}_3)_2$. The lighter lines were obtained by interpolation of the experimental data. The dotted line to the left is the lower limit beyond which the linear relation could not exist since all lines must merge at (0,0). Values in this region were not used in the calculations. Continuing with the above sample calculation;

Cd Calculations 16-1, stage 2

The distribution coefficient for the stage in consideration was computed by determining the equilibrium conditions from Plate VII using the calculated concentrations of the cadmium and copper nitrates in the stage above,

$$\text{Cd, } Y_t = 0.00215 \text{ gm/ml}$$

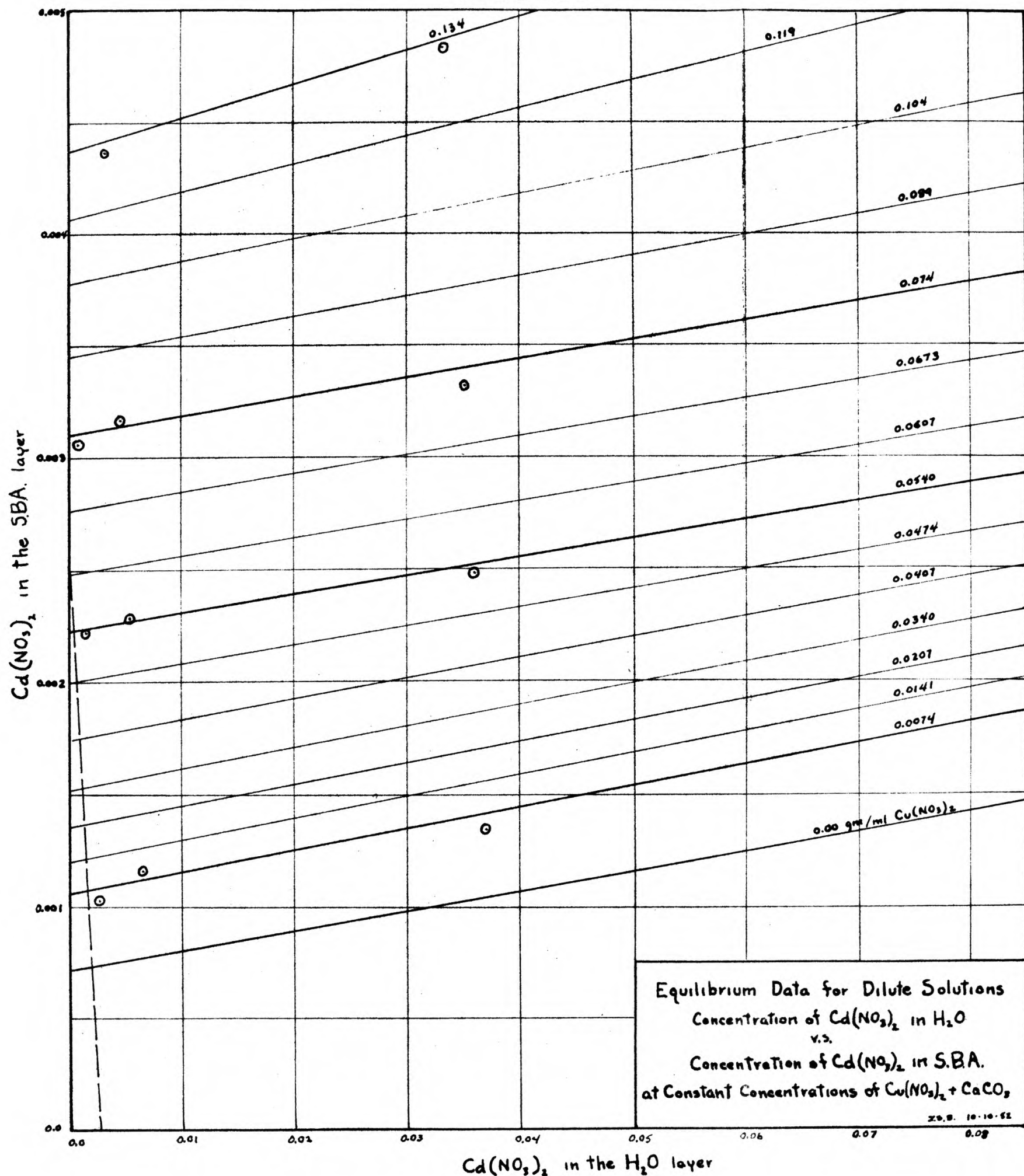
$$\text{Cu, } Y_t = 0.00317 \text{ gm/ml}$$

$$D_e = \frac{0.00215}{0.00215 + 0.00047} = 0.80, \text{ using equation (1),}$$

$$Y_2 = \frac{A^x - 1}{A - 1} Y_t = 1.97 (0.00215) = 0.00424 \text{ gm Cd/ml SBA}$$

EXPLANATION OF PLATE VII

Equilibrium Data for Dilute Solutions
with Constant Concentrations of $\text{Cu}(\text{NO}_3)_2 + \text{CaCO}_3$
Concentration of $\text{Cd}(\text{NO}_3)_2$ in H_2O
versus
Concentration of $\text{Cd}(\text{NO}_3)_2$ in SBA



calculating for the lower stage 2 using equation (2),

$$\text{Cd, } X_B = 0.00196 \text{ gm/ml}$$

$$\text{Cu, } X_B = 0.00705 \text{ gm/ml}$$

$$\text{Cu, } X_2 = 0.01090 \text{ gm/ml}$$

$$D_f = \frac{0.00115}{0.00105} = 1.095$$

$$X_2 = \frac{B^x-1}{B-1} X_B = 1.01 (0.00196) = 0.00199 \text{ gm Cd/ml H}_2\text{O}$$

From the equilibrium diagram (Plate VII) a value in gm Cd/ml SBA was found which corresponded to the value for $X_1 = 0.00196$ gm Cd/ml H_2O . When this value was multiplied by $B^x-1/B-1$, and the results (x') plotted with the stage concentration of cadmium above the feed, the intersection indicated the theoretical stage at which the feed should enter, according to equilibrium data (Plate VIII). The theoretical stage efficiencies were then calculated for the eight runs by dividing the number of theoretical equilibrium stages needed for cadmium and copper separation plus one for the feed, by the actual number of stages used (Plate VIII).

For run 13-1

$$\text{T.S.E.} = \frac{2(7.1)+1}{15} = 101\%$$

For run 13-2

$$\text{T.S.E.} = \frac{2(6.4)+1}{15} = 92.0\%$$

In a similar manner, plots were constructed for each of the other runs and the T.S.E. values (Table 6).

Theoretical stage efficiency values greater than 100% are possible in this type of calculation since the reference for 100% efficiency would be fifteen individual equilibrium stages each

thoroughly mixed and allowed to separate into their two phases, independently, in an infinite duration of time. The mechanical mixing between the stages and the countercurrent flow through the packing section, as was pointed out by Scheibel (18), may increase the stage material balance to above normal equilibrium conditions.

EXPLANATION OF PLATE VIII

Determination
of the
Theoretical Stage Efficiency
Plotted for Runs 13-1 and 13-2

RUNS 13-1 and 13-2

DETERMINATION of the THEORETICAL STAGE EFFICIENCY

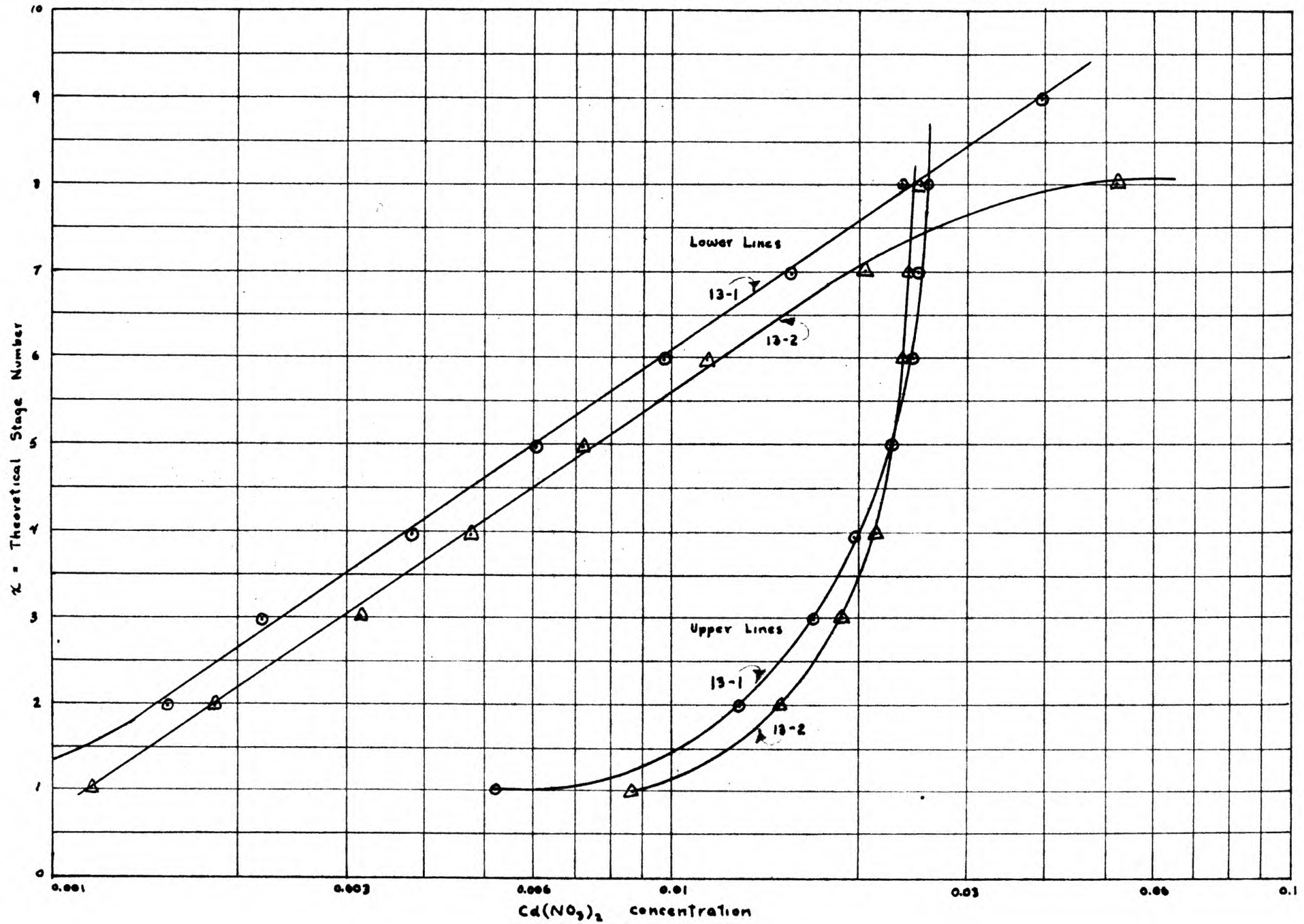


Table 6. Summary of theoretical stage efficiencies.

Run	:No. of Cd. Equil. Stages : : Needed for Separation :	Theoretical Stage Efficiency
13-1	7.1	101 %
13-2	6.4	92
14-1	9.98	139
14-2	2.45	39
15-1	4.6	68
15-2	4.4	65
16-1	10.9	152
16-2	6.7	96

CONCLUSIONS AND RECOMMENDATIONS

From the equilibrium data and Scheibel's equations for the calculation of the theoretical number of equilibrium stages, the overall theoretical stage efficiencies were determined for each run (Table 6). Three things must be remembered in the foundation of the definition for this overall efficiency.

(1) The concentration of the copper salt in the upper layer was obtained for these calculations of efficiency by the use of an average distribution coefficient obtained through single equilibrium stage data. Calculation of the copper concentration in this layer could not be determined accurately by the potentiometric method since the copper, being present in low

concentrations, precipitated along with the cadmium in the lower pH range. A gravimetric method of analysis was employed on runs 16-1 and 16-2 upper layer products and the cadmium was precipitated directly with H_2S in the presence of KCN. Subtracting from a total sulfide precipitation of the sample, the amount of copper present was determined to be,

16-1 0.00024 gm $\text{Cd}(\text{NO}_3)_2$ / ml of SBA sample

16-2 0.00015 gm $\text{Cd}(\text{NO}_3)_2$ / ml of SBA sample

Therefore, in the actual extraction, the amount of copper present in the upper product was less than 1/10 of the theoretical value calculated from single stage distribution coefficients. For Run 16-1, reduction of the upper layer products would produce a metallic cadmium with a minimum copper contamination of,

$$\frac{0.0705 (0.45) (0.10) \text{ gm Cu salt/ml SBA}}{0.00328 \text{ gm Cd salt/ml SBA}} = 0.00968 \text{ gm Cu Salt/gm Cd}$$

$$0.00968 \left(\frac{63.57}{112.4} \right) \left(\frac{236.4}{187.56} \right) = 0.0072 \text{ gm Cu metal/gm Cd metal}$$

$$\text{purity} \quad \frac{1.0000}{1.0000 + 0.0072} = 99.3\%$$

(2) Mechanical mixing with continuous flow of the immiscible solvents and the addition of an electrolyte to decrease the degree of hydration, increased the transfer rate for the column separations.

(3) Material balances around the stages assumed that the solvents to be saturated in each other throughout the column. If, however, there should be a stage in the column which (due to a high concentration of the salt or the electrolyte) does not produce

a near equilibrium stage effect, the results of the stage to stage calculations are in error. This effect is comparable to "column holdup" in distillation problems.

It might be recommended for future studies that the cadmium-zinc salt and SBA - H_2O solvent system be investigated to modify the results of this study for direct industrial applications. The column itself might be changed, with a decrease in the actual number of stages and an increase in the diameter of the column. This should prove advantageous since it was apparent through the eight runs that more calming area was needed for the subdividing of the solvents. Also, this change might allow a study of the theoretical stage efficiency as a function of the agitator speed for a wider R.P.M. range. Studies might also be made for a definite feed product, cost of solvent recovery, initial equipment cost, and locality in respect to the advantageous factors of continuous flow and high purification, for each of the many industrial applications of this extraction study.

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BIBLIOGRAPHY

- (1) Asselin, G. F., and E. W. Comings.
Fractional Solvent Extraction with Reflux. Ind. Eng. Chem.
42. 1198 (1950).
- (2) Bartels, C. R., and G. Kleiman.
Solvent Fractionation with Immiscible Solvents. Chem. Eng.
Progress 45. 589 (1949).
- (3) Bock, R., and E. Bock.
Naturwissenschaften 36. 344 (1949).
- (4) Connick, R. E., and W. H. McVey.
Chemistry of Zirconium. Journal of Amer. Chem. Soc. 71.
3182 (1949).
- (5) Fales, H., and W. Kenny.
Inorganic Quantitative Analysis, Chap. XXIV. pp. 595-600.
D. Appleton-Century Company, New York. (1939).
- (6) Fields, P.
National Nuclear Energy Service Division IV. 14-B Part II.
1128 (1949).
- (7) Fischer, W., and R. Bock.
Inorg. Chem. 249 146 (1942).
- (8) Fischer, W., and W. Chalybaeus.
(ibid) 255 79 & 227 (1947).
- (9) Garwin, L., and A. N. Hixson.
Separation of Nickel and Cobalt by Extraction from Aqueous
Solution. Ind. Eng. Chem. 41 2298 & 2303 (1949).
- (10) Geankoplis, C. J., and A. N. Hixson.
Mass Transfer Coefficients in an Extraction Spray Tower.
Ind. Eng. Chem. 42 1141 (1950).
- (11) Hixson, A. W., and M. I. Smith.
Mass Transfer in Liquid-liquid Agitation Systems. Ind. Eng.
Chem. 41 973 (1949).
- (12) Lindren W., pp. 894 and 905.
Mineral Deposits. 2nd ed. McGraw-Hill Book Company,
Inc. (1920).
- (13) McKee, R. H.
Use of Hydrotropic Solutions in Industry. Ind. Eng. Chem.
38 382 (1946).

- (14) Nachtrieb, N. H., and R. E. Fryxell.
Extraction of FeCl_3 by iso-Propyl Ether. Journ. Am. Chem. Soc. 70 3552 (1948) and 71 4035 (1949).
- (15) Nachtrieb, N. H. and J. G. Conway.
Extraction of FeCl_3 by iso-Propyl Ether. Journ. Am. Chem. Soc. 70 3547 (1948).
- (16) Norstrom, A., and L. G. Sillin.
Svensk Kem. Tid. 60 227 (1948).
- (17) Perry, J. H.
Chemical Engineers' Handbook, 3rd ed., McGraw-Hill Book Company, Inc., (1950).
- (18) Scheibel, Edward G.
Fractional Liquid Extraction Part I and Part II. Chem. Eng. Progress 44 681 (1948) and 44 771 (1948).
- (19) Siedell, A.
Solubilities of Inorganic and Metal Organic Compounds. Vol. I 3rd ed., D. Van Nostrand Company, Inc., New York, (1940).
- (20) Siedell, A.
Solubilities of Organic Compounds. Vol. 2. 3rd ed., D. Van Nostrand Company, Inc., New York, (1940).
- (21) Templeton, C. C.
Distribution of Rare Earth Nitrates between H_2O and Hexanol. Journ. Am. Chem. Soc. 71 2187 (1949).
- (22) Templeton, C. C., and J. A. Peterson.
Fractionation of La and Nd Nitrates by Solvent Extraction. Journ. Am. Chem. Soc. 70 3967 (1948).
- (23) Templeton, C. C., B. F. Rothschild, and N. F. Hall.
Distribution of $\text{Th}(\text{NO}_3)_4$ between H_2O and the esters. Journ. Phys. and Colloid Chem. 53 838 (1949). Mention is made to the alcohols and ethers.
- (24) Weinhardt, A. E., and A. N. Hixson.
Separation of Chromium and Vanadium Salts by Liquid-Liquid Extraction. Ind. Eng. Chem. 43 1676 (1951).

A P P E N D I X

Overall Material Balance
on a Weight Percent Basis for Run 16-1

Using Distribution Coefficients

Upper Layer

$$\text{Cu Salt/sec} = 0.00317 \text{ gm/ml} (2.29) \text{ ml/sec} = 0.00725 \text{ gm/sec}$$

$$\text{Cd Salt/sec} = 0.00215 \text{ gm/ml} (2.29) \text{ ml/sec} = 0.00492 \text{ gm/sec}$$

Lower Layer

$$\text{Cu Salt/sec} = 0.00705 \text{ gm/ml} (1.775+0.1) \text{ ml/sec} = 0.01320 \text{ gm/sec}$$

$$\text{Cd Salt/sec} = 0.00196 \text{ gm/ml} (1.775+0.1) \text{ ml/sec} = 0.00367 \text{ gm/sec}$$

Weight percentage indicating the degree of extraction

$$\% \text{ Cd into the upper layer} = \frac{0.00492}{0.00859} (100) = 57.4\%$$

$$\% \text{ Cd into the lower layer} = \frac{0.00367}{0.00859} (100) = 42.6\%$$

$$\% \text{ Cu into the upper layer} = \frac{0.00725}{0.02045} (100) = 35.4\%$$

$$\% \text{ Cu into the lower layer} = \frac{0.01320}{0.02045} (100) = 64.5\%$$

Using Actual Composition

Since the value of 0.00215 gm Cu Salt/ml of SBA was obtained by using the average (D) 0.45 as explained on page 28, the Cu percentages were recomputed using the actual amount for this Run as calculated by precipitation methods (see pages 41 and 42).

$$\text{Cu into the upper layer} = \frac{0.00024}{0.01344} (100) = 1.78\%$$

$$\text{Cu into the lower layer} = \frac{0.01320}{0.01344} (100) = 98.22\%$$

Run 13-1 36 ml	ml	pH	Run 13-2 20 ml	ml	pH	Run 14-1 20 ml	ml	pH	Run 14-2 20 ml	ml	pH	Run 15-1 20 ml	ml	pH	Run 15-2 20 ml	ml	pH	Run 16-1 39.75 ml	ml	pH	Run 16-2 39.5 ml	ml	pH
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TABLE 2

Lower layer titrations

Run 13-1 35 ml		Run 13-2 20 ml		Run 14-1 20 ml		Run 14-2 20 ml		Run 15-1 20 ml		Run 15-2 20 ml		Run 16-1 39.75 ml		Run 16-2 39.5 ml	
ml	pH	ml	pH	ml	pH	ml	pH	ml	pH	ml	pH	ml	pH	ml	pH
0.00	1.75	0.00	0.89	0.00	1.90	0.00	1.17	0.00	1.03	0.00	0.89	0.00	1.42	1.00	1.29
0.50	1.88	1.00	0.94	1.00	2.20	1.00	1.23	1.00	1.11	1.00	0.90	1.00	1.49	2.00	1.39
1.00	2.00	2.00	1.00	1.30	2.28	2.00	1.32	2.00	1.20	2.00	0.95	2.00	1.58	3.00	1.46
1.50	2.14	3.00	1.09	1.50	2.38	2.50	1.38	3.00	1.29	3.00	1.00	2.50	1.62	4.00	1.53
2.00	2.25	4.00	1.13	1.80	2.49	3.00	1.40	4.00	1.40	4.00	1.05	3.00	1.57	5.00	1.64
2.30	2.30	5.00	1.18	2.00	2.61	3.60	1.46	5.00	1.52	5.00	1.09	3.50	1.70	6.00	1.73
2.50	2.32	6.00	1.22	2.30	2.72	4.00	1.50	6.00	1.75	6.00	1.15	4.00	1.75	7.00	1.87
2.90	2.35	7.00	1.27	2.50	2.80	4.60	1.57	7.00	2.09	7.00	1.19	4.50	1.79	7.50	1.97
3.30	2.38	8.00	1.32	2.70	2.90	5.00	1.60	7.50	2.35	8.00	1.21	5.00	1.82	8.00	2.07
3.60	2.42	9.00	1.36	3.00	3.01	5.50	1.67	8.00	2.73	9.00	1.27	5.50	1.89	8.50	2.19
3.90	2.46	10.00	1.44	3.30	3.20	6.00	1.72	8.30	2.96	10.00	1.31	6.00	1.95	9.00	2.32
4.30	2.48	11.00	1.50	3.50	3.27	6.40	1.77	8.60	3.10	11.00	1.38	6.50	1.99	9.40	2.46
4.80	2.60	12.00	1.55	3.80	3.36	6.90	1.82	8.90	3.30	12.00	1.42	7.00	2.01	9.80	2.60
5.20	2.72	13.00	1.64	4.00	3.40	7.40	1.90	9.00	3.38	13.00	1.49	7.50	2.08	10.20	2.80
5.50	2.80	14.00	1.72	4.30	3.48	7.90	1.95	9.40	3.54	14.00	1.57	8.00	2.16	10.50	2.94
5.80	3.12	15.00	1.80	4.50	3.53	8.50	2.01	9.80	3.69	15.00	1.64	8.50	2.23	10.70	3.08
6.20	3.25	16.00	1.92	4.80	3.60	9.00	2.08	10.00	3.75	16.00	1.72	9.00	2.33	11.00	3.21
6.50	3.48	17.00	2.06	5.00	3.62	9.30	2.10	10.40	3.84	17.00	1.86	9.50	2.43	11.20	3.31
6.80	3.50	17.50	2.13	5.30	3.69	9.50	2.11	10.80	3.95	18.00	2.00	10.00	2.63	11.50	3.40
7.20	3.76	18.00	2.22	5.50	3.72	10.00	2.15	11.00	4.00	19.00	2.21	10.30	2.76	11.80	3.51
7.40	3.79	18.50	2.32	5.80	3.78	10.50	2.20	11.40	4.10	19.50	2.36	10.50	2.88	12.00	3.58
7.80	4.02	19.00	2.43	6.20	3.86	11.00	2.24	11.80	4.20	20.00	2.52	10.70	3.00	12.40	3.68
8.00	4.12	19.50	2.53	6.50	3.92	11.40	2.24	12.00	4.22	20.50	2.73	11.00	3.19	12.80	3.77
8.20	4.27	20.00	2.64	6.70	3.96	11.80	2.26	12.40	4.30	21.00	2.99	11.20	3.32	13.00	3.81
8.50	4.52	20.50	2.75	7.00	4.01	12.30	2.23	12.80	4.38	21.20	3.12	11.50	3.49	13.50	3.92
8.80	4.90	21.00	2.84	7.50	4.17	13.00	2.31	13.00	4.45	21.50	3.25	11.70	3.60	14.00	4.01
8.90	5.02	21.50	2.92	8.00	4.26	14.00	2.37	13.50	4.55	21.70	3.32	12.00	3.75	14.50	4.10
9.00	5.19	22.00	3.02	8.50	4.38	15.00	2.43	14.00	4.69	22.00	3.40	12.20	3.82	15.00	4.19
9.10	5.28	22.50	3.14	9.00	4.49	16.00	2.51	14.50	4.80	22.40	3.53	12.50	3.91	15.50	4.27
9.20	5.34	23.00	3.20	9.50	4.62	17.00	2.67	15.00	5.01	22.80	3.67	12.80	4.01	16.00	4.35
9.40	5.58	23.50	3.39	10.00	4.76	18.00	2.89	15.50	5.27	23.00	3.70	13.00	4.08	16.50	4.42
9.50	5.62	24.00	3.54	10.50	4.99	18.80	3.09	16.00	5.63	23.20	3.75	13.40	4.18	17.00	4.49
9.60	5.72	24.40	3.67	11.00	5.26	19.50	3.25	16.50	5.00	23.50	3.81	13.80	4.29	17.50	4.59
9.70	5.79	24.80	3.72	11.50	5.51	20.30	3.39	17.00	6.38	23.70	3.85	14.20	4.38	18.00	4.69
9.80	5.86	24.80	3.78	12.00	5.84	21.00	3.49	17.50	6.94	24.00	3.90	14.60	4.45	18.50	4.79
10.00	5.99	25.00	3.81	12.50	6.23	21.50	3.55	18.00	7.40	24.30	3.95	15.00	4.52	19.00	4.80
10.50	6.12	25.30	3.88	12.80	6.45	22.00	3.61	18.50	7.66	24.60	4.03	15.50	4.61	19.50	5.01
10.40	6.27	25.70	3.96	13.20	6.75	22.50	3.67	19.00	7.89	25.00	4.07	16.00	4.71	20.00	5.15
10.60	6.35	26.00	4.02	13.50	6.90	23.00	3.73	19.50	8.01	25.40	4.10	16.50	4.81	20.50	5.26
10.80	6.47	26.40	4.11	14.00	7.13	23.50	3.82	20.00	8.14	26.00	4.21	17.00	4.91	20.80	5.48
11.00	6.63	26.80	4.19	14.40	7.30	24.00	3.91	20.50	8.28	26.50	4.29	17.50	5.02	21.20	5.70
11.20	6.70	27.20	4.27	14.80	7.41	24.50	4.00	21.00	8.39	27.00	4.35	18.00	5.14	21.50	5.89
11.30	6.71	27.50	4.32	15.20	7.61	25.00	4.06	21.50	8.49	27.50	4.42	18.30	5.21	21.80	6.02
11.50	6.72	28.00	4.40	15.50	7.60	25.50	4.15	22.00	8.59	28.00	4.51	18.50	5.32	22.10	6.13
11.50	6.80	28.40	4.48	16.00	7.71	26.00	4.25	22.50	8.70	28.50	4.59	19.00	5.44	22.50	6.30
12.00	6.83	28.80	4.36	17.00	7.39	26.50	4.35	23.00	8.80	29.00	4.68	19.20	5.52	22.80	6.41
12.20	6.88	29.20	4.64	17.30	8.01	27.00	4.42	23.50	8.90	29.50	4.76	19.50	5.69	23.00	6.49
12.50	6.93	29.60	4.72	18.20	8.08	27.50	4.52	24.00	9.02	30.00	4.87	19.80	5.83	23.40	6.70
12.80	6.99	30.00	4.80	18.50	8.11	28.00	4.62	24.50	9.15	30.50	4.99	20.00	5.99	23.80	6.97
13.00	7.05	30.40	4.90	19.00	8.19	28.50	4.71	25.00	9.30	31.00	5.11	20.30	6.17	24.00	7.06
13.40	7.15	30.80	5.02	19.50	8.26	29.00	4.83	25.50	9.49	31.50	5.30	20.50	6.28	24.50	7.29
13.80	7.21	31.20	5.13	20.00	8.34	29.50	4.95	26.00	9.75	32.00	5.55	20.80	6.40	25.00	7.45
14.20	7.27	31.60	5.28	20.50	8.42	30.00	5.01	26.50	10.07	32.50	5.86	21.00	6.51	25.50	7.61
14.70	7.35	32.00	5.45	21.00	8.52	30.50	5.10	27.25	10.51	33.10	6.19	21.30	6.62	26.00	7.71
15.00	7.38	32.40	5.58	21.50	8.61	31.00	5.13	28.00	10.09	33.60	6.41	21.50	6.76	26.50	7.79
15.50	7.42	32.80	5.89	22.00	8.70	31.50	5.23			34.00	6.71	21.80	6.99	27.00	7.91
16.10	7.48	33.20	6.09	22.50	8.80	32.00	5.31			34.50	7.05	22.00	7.11	27.50	7.99
16.60	7.52	33.60	6.26	23.00	8.89	32.70	5.42			35.00	7.38	22.50	7.51	28.00	8.05
17.00	7.56	34.00	6.35	23.50	8.99	33.30	5.59			35.50	7.57	23.00	7.78	28.50	8.13
18.00	7.62	34.40	6.51	24.00	9.10	34.00	5.75			36.00	7.70	23.50	7.97	29.00	8.19
19.00	7.69	34.80	6.64	24.50	9.23	35.00	6.08			36.50	7.82	23.80	8.03	29.50	8.24
19.80	7.73	35.20	6.74	25.00	9.40	36.00	6.43			37.00	7.94	24.00	8.11	30.00	8.30
20.70	7.78	35.60	6.82	25.50	9.59	37.00	6.75			37.50	8.02	24.30	8.19	30.50	8.36
21.50	7.80	36.00	6.91	26.00	9.80	37.50	6.85			38.00	8.10	24.60	8.26	31.00	8.40
22.30	7.82	36.40	6.99	26.50	10.01	38.00	6.98			38.50	8.18	25.00	8.33	31.60	8.47
23.00	7.82	36.80	7.08	27.00	10.20	38.50	7.09			39.00	8.20	25.40	8.45	32.00	8.49
24.00	7.86	37.20	7.11			39.00	7.17			39.50	8.24	25.90	8.50	32.50	8.52
25.00	7.89	37.60	7.17			40.00	7.31			40.00	8.32	26.50	8.59	33.00	8.57
25.80	7.91	38.00	7.21			41.00	7.46			40.50	8.40	27.00	8.66	33.50	8.61
26.60	7.94	38.50	7.26			42.00	7.58			41.00	8.42	27.50	8.71	34.00	8.68
27.40	7.98	39.00	7.32			43.00	7.60			42.00	8.56	28.00	8.78	34.50	8.71
28.30	8.00	39.40	7.37			44.00	7.75			43.00	8.68	28.50	8.82	35.00	8.75
29.00	8.02	39.80	7.40			45.00	7.81			44.00	8.75	29.00	8.89	35.50	8.79
30.00	8.08	40.20	7.41			46.00	7.90			45.00	8.85	29.50	8.94	36.00	8.82
30.90	8.12	40.60	7.46			47.00	7.97			46.00	8.98	30.00	9.01	36.50	8.88
32.00	8.18	41.50	7.43			48.00	8.02			47.00	9.14	30.50	9.08	37.00	8.92
33.00	8.22	42.00	7.49			49.00	8.11			48.00	9.29	31.00	9.13	37.50	8.97
34.00	8.23	43.00	7.53			50.00	8.17			49.00	9.49	31.50	9.20	38.00	9.00
35.00	8.34	44.10	7.58			51.00	8.23			50.00	9.72	32.00	9.26	38.00	9.10
36.00	8.39	45.00	7.59			52.00	8.31			51.00	10.06	32.50	9.32	40.00	9.20
37.00	8.45	46.00	7.60			53.00	8.35								

Run 13-1	Run 13-2	Run 14-1	Run 14-2	Run 15-1	Run 15-2	Run 16-1	Run 16-2
ml	ml	ml	ml	ml	ml	ml	ml
38 ml	20 ml	40 ml	39.25 ml	25 ml	25 ml	20 ml	20 ml
pH	pH	pH	pH	pH	pH	pH	pH
2.72	1.33	1.51	1.75	0.52	1.77	1.59	0.95
0.00	0.00	0.00	0.00	0.00	3.00	0.00	0.00

TABLE 3
Upper layer titrations

Run 13-1 36 ml		Run 13-2 20 ml		Run 14-1 40 ml		Run 14-2 39.25 ml		Run 15-1 25 ml		Run 15-2 25 ml		Run 16-1 20 ml		Run 16-2 20 ml	
ml	pH	ml	pH	ml	pH	ml	pH	ml	pH	ml	pH	ml	pH	ml	pH
0.00	2.72	0.00	1.33	0.00	1.51	0.00	1.75	0.00	0.52	3.00	1.77	0.00	1.39	0.00	0.95
0.50	2.79	1.00	1.43	1.00	1.51	0.50	1.97	1.00	0.55	3.50	1.93	1.00	1.72	1.00	1.03
1.00	3.02	2.00	1.62	2.00	1.69	0.75	2.10	2.00	0.61	4.00	2.28	2.00	2.09	2.00	1.10
1.20	3.11	3.00	1.92	3.00	2.02	0.95	2.26	3.00	0.68	4.30	2.53	2.30	2.29	3.00	1.16
1.40	3.13	3.50	2.18	3.50	2.28	1.05	2.30	4.00	0.72	4.50	2.75	2.60	2.53	4.30	1.24
1.60	3.25	4.00	2.43	3.80	2.32	1.20	2.40	5.00	0.79	4.80	2.88	2.90	2.95	5.00	1.38
1.90	3.30	4.50	2.77	3.30	2.41	1.30	2.49	6.00	0.81	5.00	2.99	3.00	3.14	6.00	1.54
2.00	3.33	5.00	3.08	4.00	2.49	1.40	2.51	7.00	0.97	5.30	3.17	3.10	3.25	7.00	1.68
2.25	3.38	5.30	3.17	4.20	2.58	1.50	2.55	8.00	1.09	5.50	3.22	3.20	3.39	8.00	1.99
2.50	3.41	5.80	3.32	4.40	2.64	1.70	2.64	9.50	1.19	5.80	3.33	3.30	3.45	8.50	2.23
2.75	3.43	6.00	3.33	4.70	2.70	2.00	2.77	10.00	1.32	6.00	3.39	3.40	3.52	9.00	2.65
3.00	3.51	6.30	3.42	5.00	2.77	2.25	2.82	11.00	1.55	6.30	3.48	3.50	3.51	9.30	2.94
3.25	3.55	6.50	3.50	5.40	2.82	2.50	2.91	12.00	1.85	6.50	3.52	3.50	3.55	9.60	3.18
3.50	3.59	6.90	3.53	5.80	2.90	2.75	2.98	13.00	2.48	7.00	3.62	3.70	3.74	10.00	3.42
3.75	3.61	7.30	3.52	6.20	2.92	3.00	3.05	14.00	2.98	7.50	3.71	3.80	3.80	10.35	3.56
4.00	3.65	7.60	3.63	6.50	3.00	3.25	3.09	14.50	3.16	8.00	3.81	3.90	3.88	10.70	3.70
4.25	3.68	8.00	3.72	7.00	3.11	3.50	3.12	15.00	3.30	8.50	3.91	4.00	3.91	11.00	3.81
4.50	3.70	8.50	3.80	7.50	3.15	3.75	3.10	15.30	3.38	9.00	4.00	4.20	4.01	11.30	3.87
4.75	3.75	9.00	3.85	8.00	3.20	4.00	3.20	15.50	3.41	9.50	4.06	4.40	4.17	11.60	4.01
5.00	3.78	9.40	3.90	8.50	3.25	4.25	3.23	15.70	3.45	10.00	4.13	4.50	4.20	12.00	4.09
5.25	3.80	9.80	3.95	9.00	3.30	4.50	3.26	15.00	3.50	11.00	4.29	4.80	4.29	12.30	4.18
5.50	3.82	10.20	4.00	10.00	3.30	4.75	3.29	16.50	3.59	12.00	4.46	5.00	4.34	12.50	4.23
5.75	3.85	10.50	4.02	11.00	3.40	5.00	3.31	17.00	3.65	13.00	4.54	5.20	4.42	12.80	4.31
6.00	3.89	11.00	4.09	12.00	3.48	5.25	3.32	17.50	3.71	14.00	4.67	5.40	4.49	13.00	4.38
6.25	3.91	11.50	4.14	13.00	3.52	5.50	3.35	18.00	3.79	15.05	5.36	5.60	4.59	13.50	4.51
6.50	3.95	12.00	4.19	14.00	3.57	6.00	3.40	18.50	3.84	16.00	5.61	5.80	4.70	14.00	4.66
6.75	3.98	12.50	4.25	15.00	3.61	6.50	3.44	19.00	3.90	17.00	10.61	6.00	4.81	14.50	4.90
7.25	4.01	13.00	4.29	16.00	3.66	7.00	3.47	19.50	3.96			6.20	4.94	15.00	5.19
7.60	4.06	13.60	4.35	17.00	3.69	7.50	3.51	20.00	4.02			6.40	5.11	15.50	5.00
8.00	4.10	14.10	4.40	18.00	3.72	8.00	3.52	21.00	4.15			6.60	5.28	16.00	6.31
8.50	4.15	14.50	4.45	19.00	3.77	8.50	3.54	22.00	4.25			6.80	5.56	16.50	8.89
9.00	4.20	15.10	4.51	20.00	3.80	9.00	3.58	23.00	4.37			7.00	5.68	17.00	9.55
9.50	4.26	15.30	4.57	21.00	3.84	9.50	3.53	24.00	4.50			7.20	6.37	17.50	10.03
10.00	4.31	16.00	4.61	22.00	3.88	10.00	3.60	25.00	4.65			7.40	8.90	18.00	10.29
10.50	4.36	16.50	4.59	23.00	3.91	10.50	3.62	26.00	4.61			7.60	9.31	18.50	10.45
11.00	4.41	17.00	4.75	24.00	3.94	11.00	3.64	27.00	5.09			7.80	9.85	19.00	10.55
11.50	4.47	17.50	4.83	25.00	3.98	11.50	3.66	28.00	5.59			8.00	10.10		
12.00	4.51	18.00	4.91	26.00	4.01	12.00	3.68	28.50	7.70			8.20	10.29		
13.00	4.62	18.50	5.01	27.00	4.04	12.50	3.70	29.00	9.79			8.50	10.43		
14.00	4.77	19.00	5.11	28.00	4.08	13.00	3.72	29.50	16.27			8.80	10.60		
15.00	4.83	19.50	5.20	29.00	4.12	13.50	3.74	30.00	10.49						
16.00	5.14	20.00	5.40	30.00	4.15	14.00	3.76								
16.50	5.30	20.50	5.82	31.00	4.18	14.50	3.78								
17.00	5.52	21.00	6.85	32.00	4.20	15.00	3.80								
17.50	5.88	21.40	8.25	33.00	4.22	15.50	3.82								
18.00	7.28	21.80	8.64	34.00	4.25	16.00	3.84								
18.50	8.89	22.10	8.82	35.00	4.29	16.50	3.86								
19.00	9.11	22.50	9.17	36.00	4.31	17.00	3.88								
19.50	9.55	23.00	9.90	37.00	4.35	17.50	3.90								
20.00	9.99	23.50	10.28	38.00	4.39	18.00	3.92								
20.50	10.25	24.00	10.49	39.00	4.42	18.50	3.94								
21.00	10.42	24.50	10.60	40.00	4.47	19.00	3.96								
21.50	10.54	25.00	10.67	41.00	4.51	19.50	3.98								
22.00	10.62	26.00	10.82	42.00	4.54	20.00	4.00								
		27.00	10.92	43.00	4.59	20.50	4.02								
		28.00	11.00	44.00	4.65	21.00	4.04								
				45.00	4.69	21.50	4.06								
				46.00	4.74	22.00	4.08								
				47.00	4.78	23.00	4.10								
				48.00	4.85	24.00	4.12								
				49.00	4.90	25.00	4.14								
				50.00	4.99	26.00	4.16								
				51.00	5.11	27.00	4.21								
				52.00	5.23	28.00	4.25								
				53.00	5.36	29.00	4.28								
				54.00	5.59	30.00	4.30								
				55.00	6.04	31.00	4.32								
				56.00	6.75	32.00	4.35								
				56.15	9.55	33.00	4.39								
				56.40	9.85	34.00	4.42								
				57.00	10.06	35.00	4.45								
						36.00	4.48								
						37.00	4.51								
						37.50	4.53								
						52.00	5.00								
						53.00	5.09								
						54.00	5.17								
						55.00	5.23								
						56.00	5.29								
						57.00	5.39								
						58.00	5.50								
						59.00	5.66								
						60.00	5.97								
						61.00	6.28								
						62.00	6.42								
						63.00	9.47								
						64.00	9.90								
						65.00	10.11								

A^x	A^{x-1}	A^{x-1}	Y	B^x	B^{x-1}	X
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TABLE 4

X and Y Calculations for Cu

<u>13-1</u>	A^x	A^{x-1}	$\frac{A^x-1}{A-1}$	Y	B^x	B^{x-1}	$\frac{B^x-1}{B-1}$	X
x								
1	1.403	0.403	1.00	0.00232	0.654	-0.346	1.00	0.00582
2	1.970	0.970	2.41	0.00531	0.428	-0.572	1.652	0.0096
3	2.765	1.765	4.38	0.01144	0.280	-0.720	2.08	0.0121
4	3.89	2.89	7.18	0.01878	0.163	-0.817	2.36	0.0137
5	5.44	4.44	11.02	0.02884	0.120	-0.880	2.54	0.01475
6	7.84	6.84	18.56	0.04325	0.078	-0.922	2.66	0.01545
7	10.72	9.72	24.15	0.0631	0.051	-0.949	2.74	0.0159
8	15.10	14.10	35.0	0.0916	0.033	-0.967	2.79	0.0162

13-2

x								
1	1.370	0.370	1.00	0.00512	0.668	-0.332	1.00	0.01137
2	1.377	0.877	2.37	0.01212	0.446	-0.554	1.67	0.01897
3	2.57	1.57	4.24	0.0217	0.298	-0.702	2.11	0.02398
4	3.52	2.52	6.71	0.03428	0.199	-0.801	2.41	0.0274
5	4.82	3.82	10.31	0.0527	0.133	-0.867	2.61	0.0296
6	6.60	5.60	15.15	0.0774	0.089	-0.911	2.74	0.0311
7	9.05	8.05	21.70	0.1110	0.059	-0.941	2.84	0.0322
8	12.38	11.38	30.70	0.1570	0.039	-0.961	2.90	0.0329

14-1

x								
1	1.479	0.479	1.00	0.00417	0.605	-0.395	1.00	0.00929
2	2.185	1.185	2.47	0.01030	0.386	-0.614	1.605	0.01490
3	3.23	2.23	4.55	0.01940	0.2215	-0.7785	1.972	0.0183
4	4.78	3.78	7.90	0.03295	0.1340	-0.866	2.194	0.0204
5	7.08	6.08	12.70	0.0530	0.081	-0.919	2.326	0.0216
6	10.44	9.44	19.70	0.08225	0.049	-0.951	2.410	0.0224
7	15.43	14.43	30.1	0.1251	0.029	-0.971	2.45	0.0228
8	22.85	21.85	45.8	0.1910	0.018	-0.982	2.49	0.0231

14-2

x								
1	1.365	0.365	1.00	0.00818	0.559	-0.441	1.00	0.01815
2	1.365	0.865	2.37	0.01933	0.434	-0.566	1.66	0.0305
3	2.545	1.545	4.23	0.03450	0.286	-0.714	2.09	0.0379
4	3.48	2.48	6.90	0.05549	0.168	-0.832	2.38	0.0432
5	4.75	3.75	10.27	0.0832	0.124	-0.876	2.57	0.0468
6	6.49	5.49	15.05	0.1229	0.082	-0.918	2.69	0.0488
7	8.86	7.86	21.55	0.1753	0.054	-0.946	2.77	0.0502
8	12.16	11.16	30.40	0.2481	0.035	-0.965	2.83	0.0513

15-1

x								
1	1.248	0.248	1.00	0.0037	0.7105	-0.2895	1.00	0.00838
2	1.555	0.555	2.24	0.0083	0.505	-0.495	1.71	0.01432
3	1.940	0.940	3.79	0.0140	0.359	-0.641	2.215	0.01855
4	2.42	1.42	5.73	0.0208	0.255	-0.745	2.57	0.02154
5	3.08	2.08	8.39	0.0310	0.1812	-0.8188	2.83	0.02370
6	3.76	2.76	11.12	0.0411	0.129	-0.871	3.08	0.02520
7	4.69	3.69	14.88	0.0550	0.0910	-0.9184	3.17	0.02655
8	5.85	4.85	19.55	0.0722	0.065	-0.935	3.23	0.02706

15-2

x								
1	1.248	0.248	1.00	0.00569	0.7105	-0.2895	1.00	0.01256
2	1.555	0.555	2.24	0.01335	0.505	-0.495	1.71	0.02157
3	1.940	0.940	3.79	0.0226	0.359	-0.641	2.215	0.0281
4	2.42	1.42	5.73	0.0342	0.255	-0.745	2.57	0.0325
5	3.08	2.08	8.39	0.0500	0.1812	-0.8188	2.83	0.0359
6	3.76	2.76	11.12	0.0663	0.129	-0.871	3.08	0.0390
7	4.69	3.69	14.88	0.0865	0.0915	-0.9184	3.17	0.0402
8	5.85	4.85	19.55	0.1163	0.065	-0.935	3.23	0.0409

16-1

x								
1	1.722	0.722	1.00	0.00317	0.546	-0.454	1.00	0.00705
2	2.970	1.970	2.73	0.00865	0.298	-0.702	1.545	0.01090
3	5.115	4.115	5.70	0.01805	0.163	-0.837	1.845	0.01300
4	8.82	7.82	10.82	0.0343	0.089	-0.911	2.008	0.01414
5	15.2	14.2	19.65	0.0623	0.048	-0.952	2.097	0.01475
6	26.2	25.2	34.9	0.1105	0.026	-0.974	2.145	0.01510
7	45.2	44.2	61.1	0.1935	0.014	-0.986	2.173	0.01530
8	77.8	76.8	106.2	0.3370	0.008	-0.992	2.185	0.01540

16-2

x								
1	1.722	0.722	1.00	0.00147	0.546	-0.454	1.00	0.00328
2	2.970	1.970	2.73	0.00401	0.298	-0.702	1.545	0.00507
3	5.115	4.115	5.70	0.00837	0.163	-0.837	1.845	0.00605
4	8.82	7.82	10.82	0.01595	0.089	-0.911	2.008	0.00658
5	15.2	14.2	19.65	0.0289	0.048	-0.952	2.097	0.00687
6	26.2	25.2	34.9	0.0514	0.026	-0.974	2.145	0.00703
7	45.2	44.2	61.1	0.0900	0.014	-0.986	2.173	0.00712
8	77.8	76.8	106.2	0.1565	0.008	-0.992	2.185	0.00717

<u>13-1</u>	D_e	A^x	A^{x-1}
x			
1	0.783	0.828	-0.172
2	0.827	0.572	-0.428
3	0.832	0.435	-0.565
4	0.837	0.334	-0.666
5	0.844	0.235	-0.765
6	0.836	0.185	-0.815
7	0.815	0.168	-0.832
8	0.805	0.150	-0.85
9	0.800	0.119	-0.881

13-2

x			
1	0.900	0.685	-0.315
2	0.88	0.490	-0.510
3	0.875	0.349	-0.651
4	0.873	0.249	-0.751
5	0.855	0.191	-0.809
6	0.825	0.169	-0.831
7	0.800	0.160	-0.84
8	0.780	0.152	-0.849

14-1

x			
1	0.733	0.902	-0.098
2	0.743	0.790	-0.210
3	0.794	0.689	-0.311
4	0.780	0.528	-0.472
5	0.750	0.540	-0.460
6	0.735	0.548	-0.452
7	0.750	0.425	-0.575
8	0.750	0.376	-0.624
9	0.750	0.333	-0.667
10	0.750	0.314	-0.686

14-2

x			
1	0.874	0.704	-0.296
2	0.918	0.449	-0.551
3	0.912	0.397	-0.603
4	0.887	0.231	-0.769
5	0.865	0.182	-0.818
6	0.850	0.144	-0.856
7	0.830	0.122	-0.878
8	0.810	0.111	-0.889

TABLE 5

X, X' and Y Calculations for Cd

<u>13-1</u>	D_e	A^x	A^{x-1}	$\frac{A^{x-1}}{A-1}$	Y	D_e	B^x	B^{x-1}	$\frac{B^{x-1}}{B-1}$	X in H_2O	Calc. X'
x											
1	0.783	0.828	-0.172	1.00	0.00513	1.15	1.560	0.560	1.00	0.00053	0.00053
2	0.827	0.572	-0.428	2.49	0.01275	1.17	2.39	1.39	2.36	0.00153	0.00153
3	0.832	0.435	-0.565	3.28	0.01685	1.06	3.69	2.65	4.01	0.00213	0.00213
4	0.837	0.334	-0.666	3.77	0.01985	1.07	5.03	4.33	7.32	0.00338	0.00338
5	0.844	0.235	-0.765	4.45	0.0228	1.05	6.40	7.40	11.2	0.00594	0.00594
6	0.836	0.185	-0.815	4.74	0.0243	1.05	12.85	11.35	17.95	0.00951	0.00951
7	0.815	0.168	-0.832	4.84	0.0248	1.05	19.70	18.7	28.4	0.0151	0.0151
8	0.805	0.150	-0.85	4.94	0.0253	1.05	30.3	29.3	44.4	0.0235	0.0235
9	0.800	0.119	-0.881	5.11	0.0262	1.05	45.1	45.1	68.3	0.0398	0.0398

13-2

x											
1	0.900	0.685	-0.315	1.00	0.00901	1.532	2.275	1.275	1.00	0.00298	0.00115
2	0.88	0.490	-0.510	1.52	0.01460	1.19	3.04	2.04	1.60	0.00477	0.00184
3	0.875	0.349	-0.651	2.07	0.01855	1.11	4.48	3.48	3.73	0.00814	0.00314
4	0.873	0.249	-0.751	2.33	0.0215	1.06	6.15	5.15	4.14	0.01205	0.00476
5	0.855	0.191	-0.809	2.57	0.0232	1.04	8.00	7.80	6.12	0.01825	0.00704
6	0.829	0.169	-0.831	2.64	0.0233	1.04	13.6	12.6	9.89	0.02942	0.01135
7	0.800	0.160	-0.84	2.67	0.0241	1.06	24.0	23.0	18.05	0.0537	0.02073
8	0.780	0.152	-0.849	2.69	0.0243	1.12	54.9	57.9	48.4	0.1352	0.0522

14-1

x											
1	0.733	0.802	-0.098	1.00	0.0145	1.52	2.11	1.11	1.00	0.00422	0.00112
2	0.743	0.790	-0.210	2.14	0.0311	1.192	2.57	1.57	1.115	0.00587	0.00158
3	0.794	0.589	-0.411	4.20	0.0608	1.170	3.88	2.88	2.59	0.01095	0.00290
4	0.780	0.528	-0.472	4.82	0.0698	1.155	5.31	4.31	4.34	0.01830	0.00488
5	0.750	0.540	-0.460	4.70	0.0682	1.145	8.65	7.65	6.89	0.0291	0.00771
6	0.735	0.548	-0.452	4.61	0.0687	1.135	12.80	11.80	10.51	0.0448	0.01190
7	0.750	0.425	-0.575	5.86	0.0850	1.130	18.20	17.20	15.5	0.0653	0.01735
8	0.750	0.376	-0.534	6.37	0.0933	1.130	28.4	27.4	24.7	0.1040	0.0277
9	0.750	0.333	-0.667	6.79	0.0983	1.130	43.2	42.2	38.0	0.1600	0.0425
10	0.750	0.314	-0.686	7.00	0.1003	1.130	65.6	64.6	58.3	0.248	0.0653

14-2

x											
1	0.874	0.704	-0.296	1.00	0.0172	1.75	2.56	1.56	1.00	0.00822	0.00140
2	0.918	0.449	-0.551	1.86	0.0321	1.192	2.75	1.75	1.12	0.00922	0.00157
3	0.912	0.307	-0.693	2.34	0.0402	1.120	4.36	3.36	2.15	0.01730	0.00301
4	0.887	0.231	-0.769	2.60	0.0447	1.13	8.91	7.91	5.08	0.0416	0.00707
5	0.865	0.182	-0.818	2.76	0.0475	1.13	12.25	11.25	7.22	0.0591	0.01010
6	0.850	0.144	-0.856	2.89	0.0497	1.10	16.77	15.7	10.68	0.0826	0.01416
7	0.830	0.122	-0.878	2.97	0.0511	1.11	29.8	28.8	18.4	0.1515	0.02575
8	0.810	0.111	-0.889	3.01	0.0517	1.10	47.8	46.8	30.0	0.2464	0.04200

<u>15-1</u>	De	A ^x	A ^{x-1}	$\frac{A^x-1}{A-1}$	Y	Df	B ^x	B ^{x-1}	$\frac{B^x-1}{B-1}$	X in H ₂ O	Calc. X'
x											
1	0.890	0.63	-0.37	1.00	0.00526	1.23	2.39	1.39	1.00	0.00433	0.00115
2	0.895	0.394	-0.606	1.34	0.01025	1.085	2.94	1.94	1.395	0.00604	0.00181
3	0.844	0.293	-0.707	1.91	0.01195	1.120	5.54	4.54	3.25	0.01415	0.00375
4	0.851	0.188	-0.812	2.19	0.01372	1.085	8.64	7.64	3.49	0.0238	0.00631
5	0.851	0.117	-0.883	2.33	0.01490	1.065	13.39	12.39	6.90	0.0385	0.01022
6	0.855	0.080	-0.920	2.48	0.01556	1.092	26.30	25.30	18.20	0.0787	0.02094
7	0.849	0.055	-0.945	2.58	0.0159	1.225	101.3	100.3	72.1	0.3121	0.08290
8	0.835	0.041	-0.959	2.58	0.0162						

15-2

x											
1	0.805	0.697	-0.303	1.00	0.00485	1.44	2.275	1.275	1.00	0.00544	0.00120
2	0.801	0.490	-0.510	1.58	0.00815	1.185	3.500	2.50	1.96	0.01064	0.00235
3	0.807	0.336	-0.664	2.19	0.01063	1.170	6.27	5.27	4.13	0.0224	0.00496
4	0.828	0.211	-0.789	2.60	0.0126	1.155	11.09	10.08	8.45	0.0450	0.01013
5	0.803	0.167	-0.833	2.75	0.0133	1.190	20.6	19.6	15.35	0.0835	0.01830
6	0.798	0.120	-0.88	2.91	0.0141	1.160	38.1	37.1	29.1	0.1580	0.0348
7	0.800	0.083	-0.917	3.03	0.0147	1.160	51.5	50.1	35.7	0.1995	0.0440
8	0.808	0.054	-0.946	3.13	0.0152						

16-1

x											
1	0.80	0.968	-0.032	1.00	0.00215	1.46	1.79	0.79	1.00	0.00196	0.00110
2	0.80	0.937	-0.063	1.97	0.00424	1.095	1.80	0.80	1.01	0.00199	0.00111
3	0.80	0.906	-0.094	2.94	0.00631	1.06	2.20	1.20	1.52	0.00303	0.00156
4	0.80	0.876	-0.124	3.83	0.00834	1.04	2.64	1.64	2.08	0.00412	0.00229
5	0.80	0.846	-0.154	4.81	0.01035	1.02	3.06	2.06	2.53	0.00521	0.00289
6	0.80	0.822	-0.178	5.54	0.0119	1.02	3.83	2.83	3.58	0.00708	0.00394
7	0.80	0.796	-0.204	6.33	0.0137	1.02	4.80	3.80	4.80	0.00965	0.00538
8	0.80	0.768	-0.232	7.25	0.0156	1.02	5.98	4.98	6.32	0.01250	0.00695
9	0.80	0.744	-0.256	7.94	0.0171	1.02	7.48	6.48	8.21	0.01625	0.00905
10	0.80	0.720	-0.28	8.75	0.0185	1.02	9.35	8.35	10.86	0.02085	0.01164

16-2

x											
1	0.82	0.945	-0.055	1.00	0.00328	1.14	1.35	0.35	1.00	0.00314	0.00085
2	0.80	0.937	-0.063	1.145	0.00376	1.08	1.75	0.75	2.14	0.00872	0.00182
3	0.80	0.906	-0.094	1.71	0.00554	1.06	2.31	1.31	3.74	0.01175	0.00218
4	0.80	0.876	-0.124	2.25	0.00742	1.03	2.52	1.52	4.35	0.01365	0.00370
5	0.80	0.846	-0.154	2.80	0.00918	1.03	3.18	2.18	6.23	0.01955	0.00529
6	0.80	0.822	-0.178	3.23	0.01060	1.04	4.28	3.28	9.00	0.0285	0.00772
7	0.80	0.796	-0.204	3.71	0.01215	1.04	5.46	4.46	12.78	0.0401	0.01085
8	0.80	0.768	-0.232	4.21	0.01382	1.04	6.95	5.95	17.0	0.0533	0.01445

THE SEPARATION OF CADMIUM AND COPPER SALTS
BY LIQUID-LIQUID EXTRACTION

by

JACQUES S. BOEGLI

B. S., Indiana Technical College, 1950
Fort Wayne, Indiana

AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

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KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1953

The purpose of this research study was to develop a high purity extraction process for the separation of cadmium from copper salts. From a literature survey of accomplished metallic salt extractions, it was found that a fractional liquid-liquid extractor of the multistage form could produce a highly efficient separation. A York-Schiebel, fifteen stage, countercurrent gravity flow, two inch laboratory extractor was employed in the study.

The ability to perform the necessary extraction-separation was known to be limited to the preferential solubility and the physical properties of the solvents used, and a study was made to determine the two solvents which would be most applicable. Secondary butyl alcohol was chosen as the light solvent (introduced at the bottom of the column) and water, the heavy solvent (introduced at the top). The nitrates (and also the chlorides) of cadmium and copper in aqueous solution were introduced as feed at the mid-point of the column. Agitator speeds of 150-300 R.P.M. were studied.

Independent stage calculations were made for determining the stage concentration of the salts using an equation derived by Scheibel and based on product composition, material balances around the stages, and equilibrium data. Overall theoretical stage efficiencies were determined for each of the runs (efficiencies from 39-152% were reported), and an explanation for efficiencies greater than 100% was outlined by the following:

- (a) Material balances around the stages in the calculation assumed the solvents to be fully saturated in each other.
- (b) Calculations were based on single stage equilibrium data, whereas true equilibrium conditions throughout the column were not established.
- (c) Mechanical mixing with continuous countercurrent flow and the addition of an electrolyte increased the transfer rate.

The analysis of the products in the upper layer (secondary butyl alcohol) indicated that from the dilute nitrate feed solution, the cadmium salt could be extracted and finally reduced to the metal with a purity of about 99.3%.